BICYCLO[3.2.0]HEPTA-1, 4, 6-TRIENE: SYNTHESIS, THERMAL REARRANGEMENT, AND ANION FORMATION

Thesis

by

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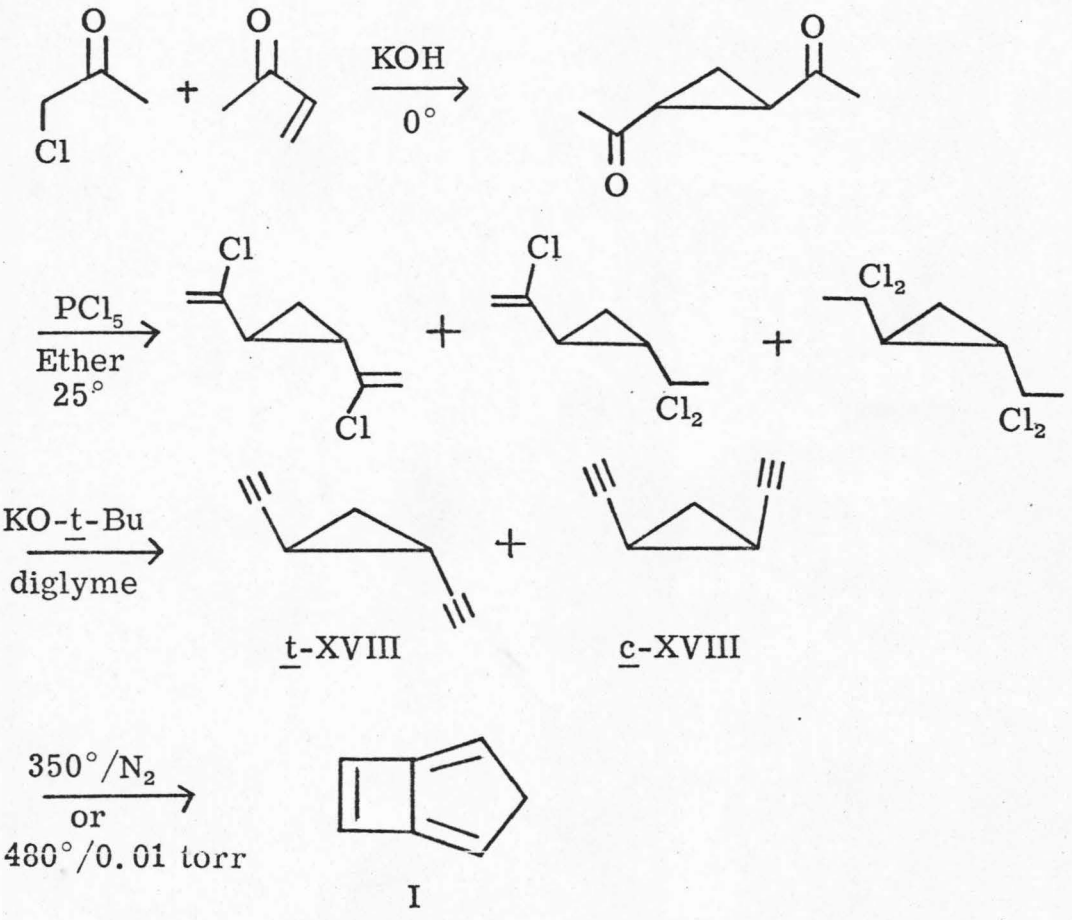
Abstract

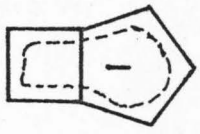
In order to determine the properties of the bicycloheptatrienyl anion (Ia) (predicted to be conjugatively stabilized by Hückel Molecular Orbital Theory) the neutral precursor, bicyclo[3.2.0]hepta-1, 4, 6-triene (I) was prepared by the following route.



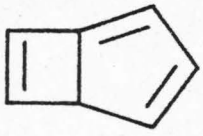
t-XVIII c-XVIII

I

Reaction of I with potassium-t-butoxide, potassium, or lithium dicyclohexylamide gave anion Ia in very low yield. Reprotonation of I was found to occur solely at the 1 or 5 position to give triene II, isolated as to its dimers.



Ia



II

A study of the acidity of I and of other conjugated hydrocarbons by means of ion cyclotron resonance spectroscopy resulted in determination of the following order of relative acidities:

$H_2S > C_5H_6 > CH_3NO_2 > 1,4\text{-}C_5H_8 > I > C_2H_5OH > H_2O$;

cyclo-$C_7H_8 > C_2H_5OH$; $\phi CH_3 > CH_3OH$

In addition, limits for the proton affinities of the conjugate bases were determined:

350 kcal/mole $<$ PA($C_5H_5^-$) $<$ 360 kcal/mole

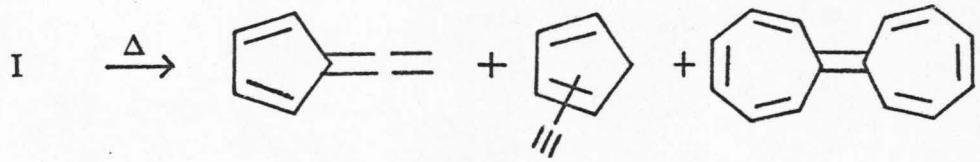
362 kcal/mole $<$ PA($C_5H_7^-$, Ia, cyclo-$C_7H_7^-$) $<$ 377 kcal/mole

PA(ϕCH_2^-) $<$ 385 kcal/mole

Gas phase kinetics of the trans-XVIII to I transformation gave the following activation parameters: E_a = 43.0 kcal/mole, log A = 15.53 and $\Delta S^{\ddagger}$ (220°) = 9.6 cu. The results were interpreted as indicating initial 1, 2 bond cleavage to give the 1, 3-diradical which

closed to I. Similar studies on cis-XVIII gave results consistent with a surface component to the reaction (E_a = 22.7 kcal/mole; log A = 9.23, $\Delta S^{\ddagger}$ (119°) = -18.9 eu).

The low pressure (0.01 to 1 torr) pyrolysis of trans-XVIII gave in addition to I, fulvenallene (LV), ethynylcyclopentadiene (LVI) and heptafulvalene (LVII). The relative ratios of the C_7H_6 isomers were found to be dependent upon temperature and pressure, higher relative pressure and lower temperatures favoring formation of I. The results were found to be consistent with the intermediacy of vibrationally excited I and subsequent reaction to give LV and LVI.



LV LVI LVII

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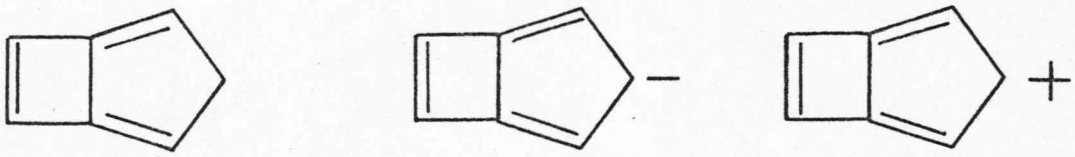
CHAPTER Ia
INTRODUCTION

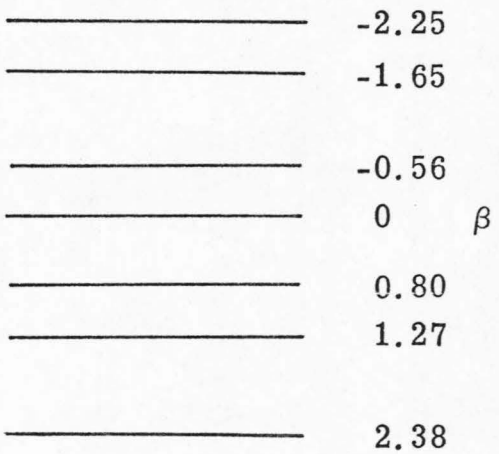
The physical organic chemistry of highly conjugated cyclic species remains the focal point of much current research (1). Except for the cyclopropenyl system (2), however, the properties of molecules which are both highly strained and conjugated are less well known. These types of molecules are of interest from both synthetic and theoretical points of view. Synthesis often requires novel techniques which have to take into account the high reactivity of strained species, whereas theoretically, opportunities arise for the study of the combination of both strain and conjugation upon physical and chemical properties.

Simple nonbenzenoid species which are both highly strained and conjugated are bicyclo[3.2.0]hepta-1, 4, 6-triene (I) and its anion Ia and cation Ib. The ions are of special interest because Hückel Molecular Orbital (HMO) theory predicts a high degree of stability for both. Although some work has been done on the anion Ia, the chemistry of these systems remains largely unknown. The remainder of this chapter describes in some detail the aspects and predictions of molecular orbital calculations for ions Ia and Ib, a possible synthetic pathway to I, and the recent work on anion Ia.



I Ia Ib

Molecular Orbital Considerations - Energetics. The HMO energy levels and π energy for the bicycloheptatrienyl system have been determined by Streitwieser and Brauman (3) and are given in Figure 1. The results of this zero order method are quite interesting. The presence of a nonbonding orbital of zero energy not present in most cyclic arrays predicts that the anion Ia and the cation Ib will have equal π energies. In order to gain insight into the stability of these ions, the π energy must be compared to that calculated for an appropriate model system. The choice of model systems depends upon the interpretation desired. The most simple and most often used is to compare the system in question to one containing the same number of, but non-interacting, double bonds and carbon 2p orbitals. In this case the model system would consist of three double bonds and a lone p orbital. The energy of delocalization by this method is calculated to be 2.90β for both ions. This value compares quite favorably to 2.99β calculated for cycloheptatrienyl cation and 2.47β calculated for cyclopentadienyl anion. Both of these monocyclic ions have been shown to be chemically quite stable (4) and the implication is that the bicyclic ions should be equally as stable.



π_e (Ia) = 8.90 β

π_e (Ib) = 8.90 β

Figure 1. Energy Levels and π Energy of Bicycloheptatrienyl

A second method of comparison determines the amount of extra stability conferred on the system by its cyclic nature. Here the appropriate model system must be structually the same but contain only bond interactions of the type found in linear polyenes. Comparison of the HMO π energy of the system in question with the π energy of its model system would give a quantitative prediction of any extra stability (aromaticity (5)). Positive differences imply the system is aromatic; negative differences imply antiaromaticity (6) while no difference implies only polyene-like interactions (nonaromaticity). Obviously the main problem in this comparative method in addition to those ignored by the Hückel method, such as strain energy, is determination of the π energy of the model system. Hess has reported such a determination but for neutral systems only (6). An extension of Hess' method was developed for charged systems and is presented in Chapter Ib.

Assuming that the property of aromaticity confers low reactivity on a system the results of the extension of Hess' method are quite reasonable chemically. For instance, in terms of Hess' definitions, the cyclopentadienyl anion is predicted to be highly aromatic (resonance energy per electron (REPE) = $+0.11\beta$) whereas the cation is predicted to be quite antiaromatic (REPE = -0.17β). These results are consistent with the known stability of the anion and the only transient existence of the cation (5). (Cyclopentadienone in which a resonance form places positive charge in the cyclopentadienyl ring can be isolated only at very low temperatures (7).) As expected

the cycloheptatrienyl system shows the opposite behavior, the cation (REPE = +0.11 β) being much more easily prepared than the anion (REPE = -0.035 β). As for the bicyclic ions Ia and Ib both are predicted to be slightly aromatic (REPE Ia = +0.015 β; REPE Ib = +0.020 β) and on the above basis are predicted to be capable of isolation.

The above methods have assumed that chemical unreactivity is an indication of electronic stability. As is pointed out in Chapter Ib this assumption may not always be valid. Perhaps in the case of the anions, stability may be best correlated with acidity of the conjugate acids (8). In other words, the heat of the ionization reaction is related to the electronic stability of the anion formed. On this basis, the modified Hess method would predict cyclopentadiene to be much more acidic than cycloheptatriene with bicycloheptatriene I lying in between. The ordering for the first two is correct while some recent results (9) of Breslow suggest that the bicyclic system is also in the correct position. To summarize, the modified Hess method predicts only a moderate amount of extra stability for the bicyclic ions compared to an acyclic polyene ion.

Validity of the HMO Method for the Bicyclic Ions. It should be pointed out here that confidence in the results of the above methods of comparison is determined by the validity of HMO theory for the systems considered. It turns out that the theory may even be less valid for the bicyclic ions than it is for monocyclic because of the non-alternant nature of their structures (10). The major

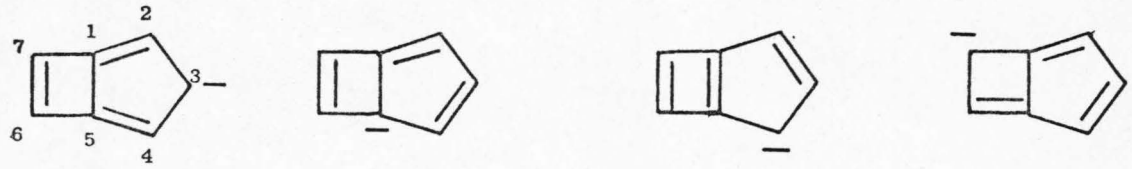
assumptions in HMO theory are that the resonance integrals are equal ($\beta_{12} = \beta_{23}$) and that the couloumb integrals are equal ($\alpha_1 = \alpha_2$) for all carbon atoms. For alternant systems, the calculated charges on the carbon atoms are equal. This fact lends support to the validity of the above assumptions. The calculations in these cases are said to be self-consistent (10). For non-alternant systems the unequal charge distribution may drastically change α from one carbon to another. The simple HMO treatment for these systems is not self-consistent. To correct for this, more sophisticated iterative calculations are required. For instance, for pentalene simple HMO treatment gives four filled bonding levels and an unoccupied nonbonding level. This array would appear to be energetically favorable. However calculations using the α, ω technique in which values for α and β are iterated until no further change in π energy is noted show that the nonbonding level becomes bonding (11). Such an array gives an unstable open shell orbital arrangement for the neutral but predicts the dianion to be closed shell and stable. Experiments bear out these predictions. The dianion salt is easily isolated (12) whereas the only known simple pentalene, methylpentalene, dimerizes at -140°(13). Thus Boyd has warned that only a slight change in the Hückel matrix will affect the energy of the nonbonding MO (11). Certainly then in the case of the bicyclic ions predictions concerning the stability of the cation vs. the anion will be at best uncertain.

A more sophisticated calculation for the anion Ia has been carried out for us by Howard E. Simmons and the text of his letter describing the results of a Self Consistent Field-Pariser-Parr-Pople calculation is reproduced in Appendix I. The calculated π bond energy was -19.824 ev or -2.478 ev per electron. The π energy per electron for a eight electron linear conjugated polyene is -2.205 ev (14). Compared to the acyclic neutral system then, anion Ia exhibits more effective π bonding.

Molecular Orbital Considerations - Charge Distribution and Bond Order. Consideration of the calculated charge distribution and bond orders are important because these properties are amenable to experimental verification. Nmr analysis (15) and reprotonation studies (16) help to determine charge densities at different carbon atoms while Ir and X-ray diffraction studies supply information on bond lengths.

The results of the HMO calculations and of the advanced SCF calculation for anion Ia surprisingly give very similar values for the charge distribution and bond orders. The most striking aspects of these calculations are the unequal distribution of charge and the localization of the cyclobutenyl double bond. The unsymmetrical charge distribution (Appendix I) may be rationalized in terms of resonance structures. Of the resonance structures drawn below the ones which place charge on the 2 or 4 positions display the energetically unfavorable cyclobutadiene moiety. The calculated charge densities reflect the unimportance of these contributors. Greater

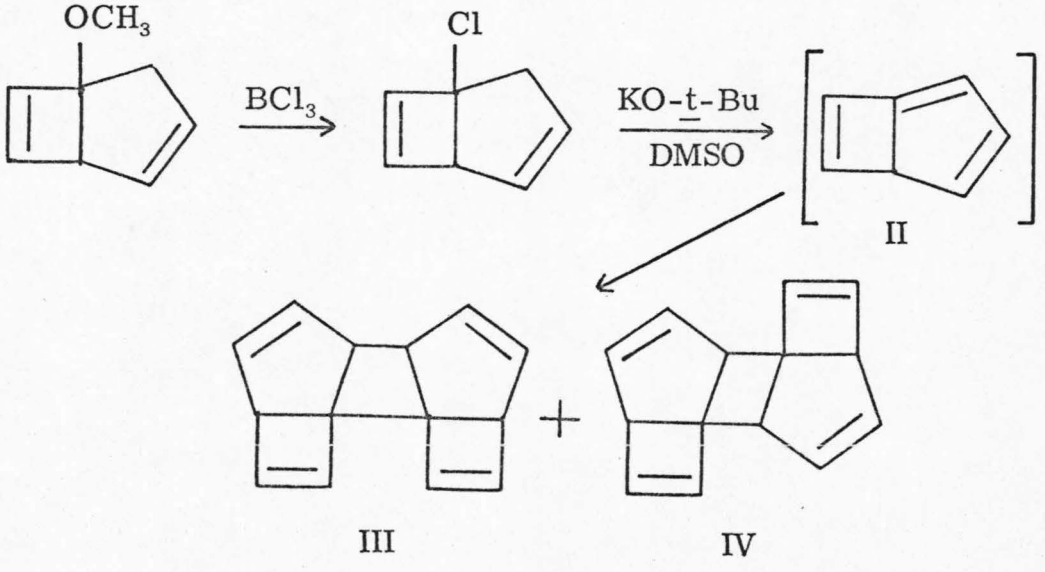
than 70% of the charge resides on the 1, 3 and 5 positions.



The high degree of double bond character in the 6, 7 linkage implies that the anion may be considered a cyclopentadienyl anion fused to a weakly interacting double bond.

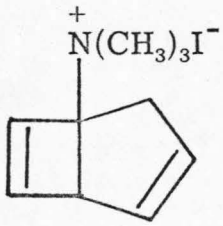
Recent Work Workers in other groups have utilized the double bond isomer of I, bicyclo[3.2.0]hepta-1, 3, 6-triene (II) as precursor to anion Ia.

Breslow was the first to report work on the synthesis of triene II (17). Transient existence of II was inferred from the isolation of the dimeric compounds III and IV from the following sequence of reactions. The highly strained triene II is unstable relative to its

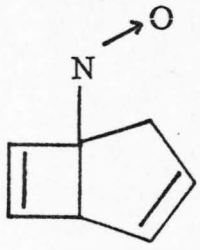


dimers, reaction taking place at the twisted bridgehead double bond. Also diphenylisobenzofuran reacts readily with II to give a Diels—Alder adduct. Under conditions of high dilution a UV spectrum of the elimination reaction mixture displayed a new band at 316 nm. The band decayed with second order kinetics and was attributed to II.

Bauld obtained dimers III and IV by the reaction of methiodide V with sodium methoxide in DMSO or by the pyrolysis of nitroxide VI at 120° (24). Triene II was intercepted with dienes diphenylisobenzofuran and cyclopentadiene but not with dienophiles dimethyl acetylenedicarboxylate or dimethyl fumarate. It was concluded that II is a very reactive dienophile.

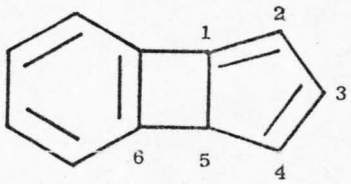


V

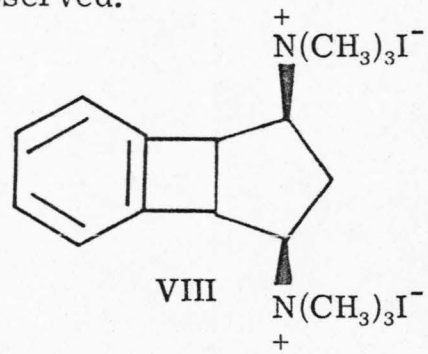


VI

Cava has studied the benzobicycloheptatrienyl system VII (18). Again, only dimers are isolated from the double elimination of trimethylammonium iodide from bis methiodide VIII. Interestingly none of the 1, 4, 6 isomer of VII was observed.



VII

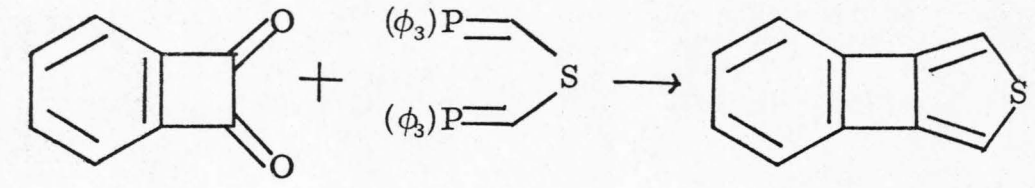


VIII

Both Breslow and Cava found that when the elimination was run with an excess of base in deuterated solvent, two deuteriums were incorporated into each dimer molecule. Both authors explained this result by postulating formation of a bicycloheptatrienyl anion by proton abstraction from the tertiary bridgehead position of triene II or VII. Apparently redeuteration takes place solely at the bridgehead position although it is possible that the 1, 4, 6 triene resulting from deuteration at the 3 position might go undetected under the reaction conditions. Both dimers and starting materials were found not to exchange protons under the reaction conditions. Bauld however observed no deuterium incorporation under the same conditions. He concluded that no anion is being formed. The reason for disagreement in results from different research groups is unknown at present.

Breslow and Washburn have assigned a pK_a to the 1, 3, 6-triene II by a series of equilibration experiments (9). By addition of carbon acids of known pK_a to a presumed dilute solution of anion Ia in tetrahydrofuran and then quenching with deuterium oxide, it was possible to determine the position of equilibrium. From the series of experiments with triphenylmethane, xanthene, and fluorene it was found that the pK_a of triene II lies close to that of xanthene (pK_a = 29). In the same medium cyclopentadiene was found to have pK_a 18. Thus the effect of the fused double bond is to raise the pK_a of the cyclopentadiene moiety by 11 pK_a units. Breslow states this effect may be due to increased strain in the bicyclic system but is also consistent with destabilization from cyclobutadienoid resonance forms.

Garrat has reported interesting results on synthesis of heteroatom derivatives of I (19). Compounds IX and X were synthesized by the indicated routes. The benzo derivative is quite stable



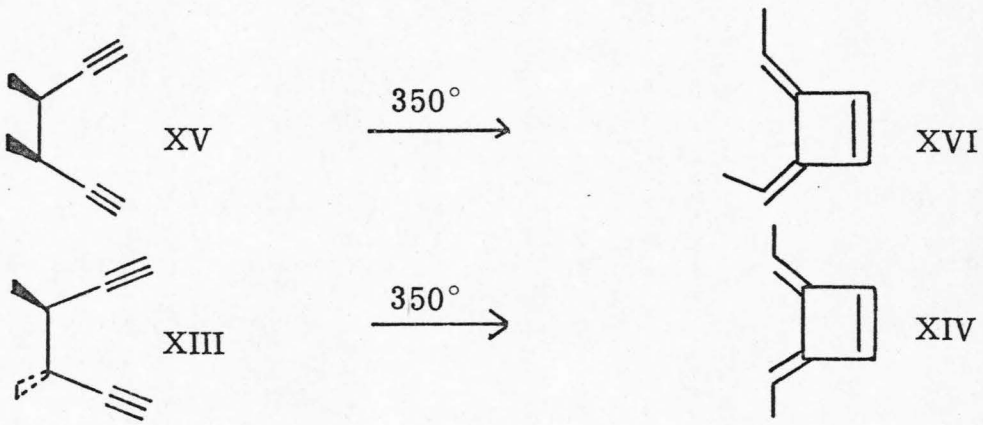
IX

X

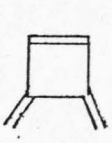
while the diphenyl derivative dimerizes slowly at room temperature. The structure of the dimer was not indicated.

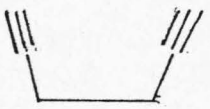
Basis for the Present Research. The rearrangement of 1, 5-hexadiyne (XI) to dimethylenecyclobutene (XII) reported by Huntsman and Wristers (20) provides the basis for the synthesis of I. The Huntsman reaction displays first order kinetics from which the following Arrhenius parameters may be derived, E_a = 34.4 kcal/mole and $\Delta S^{\ddagger}$ = -9.4 eu. The products from the rearrangement of substituted 1, 5-diynes are given below.

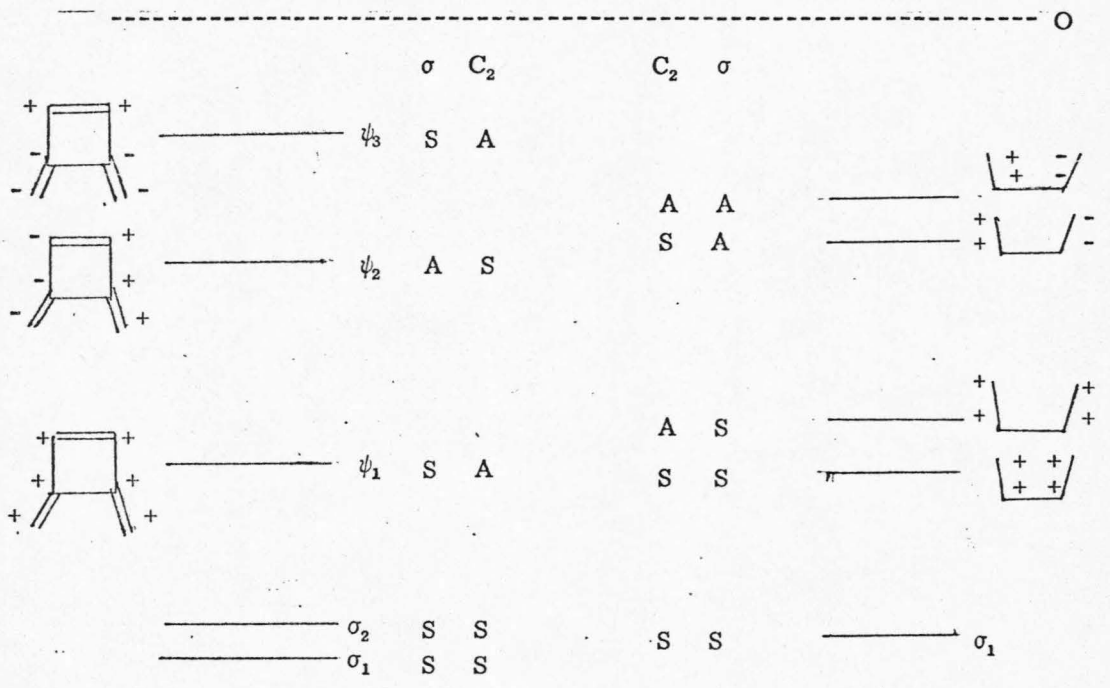
XI XII



The most striking aspect of the rearrangement is that it appears to be stereospecific. The observed stereochemistry is the result of conrotatory motion of the methyl groups during the course of the reaction. Thus rac-XIII gives solely trans, trans-XIV while meso-XV gives only cis, trans-XVI. It is reasonable to assume from the values of the Arrhenius parameters that the reaction proceeds through a cyclic transition state. The Woodward-Hoffmann treatment of concerted reactions can be applied here (21). The correlation diagram necessary for such an analysis can be constructed in a straightforward manner. The only possible ambiguity lies in the ordering of the acetylenic combinational orbitals (combinational orbitals are necessary because of the centrosymmetric nature of the acetylenic triple bond). However in the present case the relative ordering is not important because only the bonding orbitals will be considered for the thermal reaction. This treatment predicts products resulting from conrotatory motion of the methyl groups as is observed experimentally. An alternate but equivalent approach is to consider







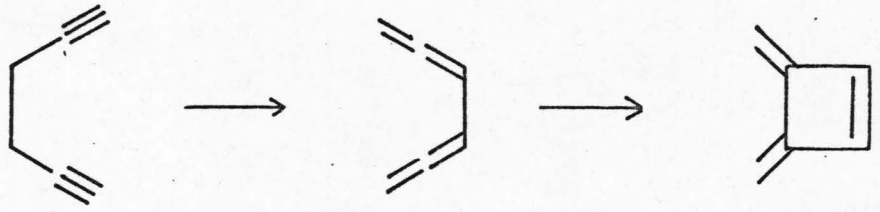
State functions

σ(dis)	$S^2S^2S^2A^2S^2$	$S^2S^2S^2A^2A^2$
C_2(con)	$S^2S^2A^2S^2A^2$	$S^2S^2A^2S^2A^2$

state functions resulting from conrotatory mode correlate.

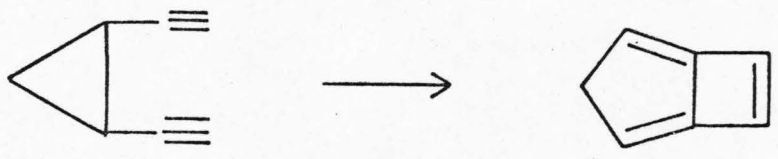
Figure 2. Correlation Diagram for the 1, 5-Hexadiyne to 3, 4-Dimethylenecyclobutene Transformation.

the rearrangement taking place in two steps, the first being a Cope-like rearrangement to diallene XVII and the second being ring closure of the butadiene portion of the diallene to a cyclobutene. The second step gives the correct stereochemistry. The diallene to dimethylene-cyclobutene rearrangement has been observed, but no studies on the stereochemistry of the reaction were reported (22).



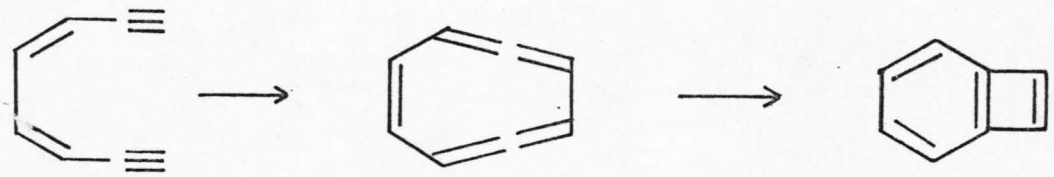
XVII

The bicyclic system I is a ring closed derivative of the cyclobutene XII, the 5, 6 exo positions having been joined by a methylene bridge. To prepare I in a manner analogous to XII would require similar bonding in the diacetylene precursor. The 3, 4 positions of diyne XI would have to be bridged by a methylene group to give 1, 2-diethynylcyclopropane (XVIII). Isomerization of cis-XVIII to I must take place with disrotatory motion of the cyclopropane group. Since the Woodward-Hoffmann allowed pathway requires



XVIII I

conrotatory motion, the concerted transformation of cis-XVIII to I might require substantial activation energy. However there are other non-concerted pathways open to these systems. Cleavage of the 1, 2 bond in either cis or trans-XVIII would give a diradical which could go to I. In this case one would expect both cis and trans-XVIII to have similar energetic requirements. Another possibility is that the non-allowed pathway may be accessible for highly energetic strained molecules. For instance, Sondheimer has observed a very fast dis closure of the butadiene group in XIX (23). This species is very similar to a possible diallene type intermediate from a Cope re-arrangement of cis-XVIII.



XIX

The goal of the present research is to synthesize cis- and trans-XVIII, to study their possible thermal rearrangement to I, and to investigate means of converting I to ionic species Ia and Ib.

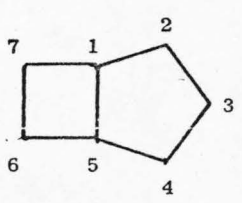
APPENDIX I

An advanced SCF-Pariser-Parr-Pople calculation has been carried out for the anion Ia by Howard E. Simmons. The outline of the method and results are quoted directly from his private communication.

> The gist of the method is that after carrying out a Pariser-Parr-Pople calculation with an assumed geometry, a new geometry is computed on the basis of the SCF bond orders along with the assumption that the total deviations of the interior ring angles from trigonal hybrids be minimized. The SCF calculation was then iterated to a stable value of the total pi electron energy. Interestingly, the calculations converged after only three iterations, and the results represent some kind of a best SCF calculation in the sense that a minimum energy geometry has been found. At this point the final wavefunctions are used to carry out a configuration-interaction calculation taking into account all singly excited configurations. The lowest singlet and triplet states with their symmetries are given below. The oscillator strengths are also given as f.

State	Energy, eV	Transition Wavelength (nm)	f
$^1A_1$	0	---	Ref.
$^1B_1$	2.157	575	.0004
$^1A_1$	4.231	293	.235
$^1A_1$	5.737	216	.717
$^1B_1$	5.980	207	.068
$^3B_1$	1.383	---	.004
$^3A_1$	2.994	---	.004
$^3A_1$	4.331	---	.038

> The final charge densities and bond orders worked out as follows:



	qi		pij
i = 1	1.217	ij = 16	0.1559
6	1.055	67	0.9369
2	1.111	15	0.5897
3	1.235	12	0.6672
		23	0.6287

The total pi energy computes to be -218.905 eV; the framework repulsion energy is +118.273 eV, so that the effective pi energy is -100.632 eV and the effective pi bond energy (relative to the valence state of carbon) is -19.824 eV.

The SCF energies are:

n =	En (eV)
1	-9.623
2	-7.193
3	-5.267
4	-3.991
5	3.698
6	6.797
7	8.114

CHAPTER Ib

CALCULATION OF RESONANCE ENERGIES FOR CYCLIC IONS

Hess has recently published a method for evaluating aromatic character in conjugated neutral systems (6). Additive energy values were assigned to the different kinds of double and single bonds found in linear and cross conjugated polyenes. The π energy for any neutral cyclic or acyclic conjugated system may then be calculated by group additivity. Resonance energy (RE) is defined as the difference between the HMO π energies and the π energy obtained by the Hess additivity method. A positive difference is associated with aromaticity, negative with antiaromaticity and zero with non-aromaticity (polyene-like). According to Hess, resonance per electron (REPE) is a better way of comparing aromaticity in molecules of different carbon number. Consider the molecules benzene and fulvene. The Hess π energies may be described by Equation (1) for benzene and Equation (2) for fulvene.

$$\pi_{e(B)} = 3(CH{=}CH) + 3(CH{-}CH) \qquad (1)$$

$$\pi_{e(F)} = 2(CH{=}CH) + (CH_2{=}C) + (CH{-}CH) + 2(CH{-}C). \qquad (2)$$

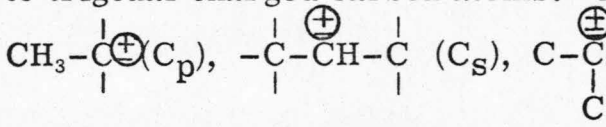
Hess' π bond energies are given in Table I.

Table I. Hess π Bond Energies

Type of Bond	Calculated π Bond Energy β
$H_2C=CH$	2.000[a]
HC=CH	2.070
$H_2C=C$	2.000[a]
HC=C	2.108
C=C	2.172
HC-CH	0.466
HC-C	0.436
C-C	0.436

[a] Arbitrarily assigned.

For benzene the Hess π energy is 7.61 β while the HMO π energy is 8.00 β. Therefore the resonance energy of benzene is 0.39 β and the REPE is 0.065 β. Likewise for fulvene the Hess π energy is 7.48 β and the HMO π energy is 7.47 β. The resonance energy is -0.01 β and the REPE is -0.002 β. Benzene is predicted to be aromatic while fulvene is predicted to be polyolefinic. By this method, Hess was able to calculate resonance energies for 64 cyclic olefins; excellent agreement between calculated resonance energy and chemical behavior was obtained.

Unfortunately, the above method has no provision for calculating energies for charged systems. In order to extend Hess' method to charged molecules it is necessary that energy values be assigned to trigonal charged carbon atoms. These are of three types:  (C_p), (C_s), (C_t), corresponding to primary, secondary and tertiary carbon ions.

My method utilizes the Hückel π energies for a series of linear polyenes, including both odd and even systems. Consider the change in π energy is going from a C_nH_{n+2} even polyene to a $C_{n+1}H_{n+3}$ charged odd polyene. In the limit as n becomes large the increase in π energy and the change in structures may be correlated with the formal insertion of a charged CH group into a carbon-carbon single bond of the C_nH_{n+2} moiety. One should expect the change in energy to become constant for large n because the perturbation to the system due to the addition of the CH moiety becomes small at large n. Since at large n the charge will have greatest density on secondary carbons, it is assumed that this constant change in energy can be assigned to the additivity for a secondary charged carbon atom (C_s). In order to ascertain if, in fact, such a constant exists, the change in π energy ($\Delta\pi_e$) was plotted against the corresponding polyene pair in Figure 3. Indeed $\Delta\pi_e$ does become constant at $1.20\,\beta$ when n = 20. This value is also obtained when n = 30. Therefore, charged secondary carbon (C_s) is assigned the additivity energy of $1.20\,\beta$. An examination of Figure 3 also shows that for n = 2, $\Delta\pi_e$ equals $0.83\,\beta$.

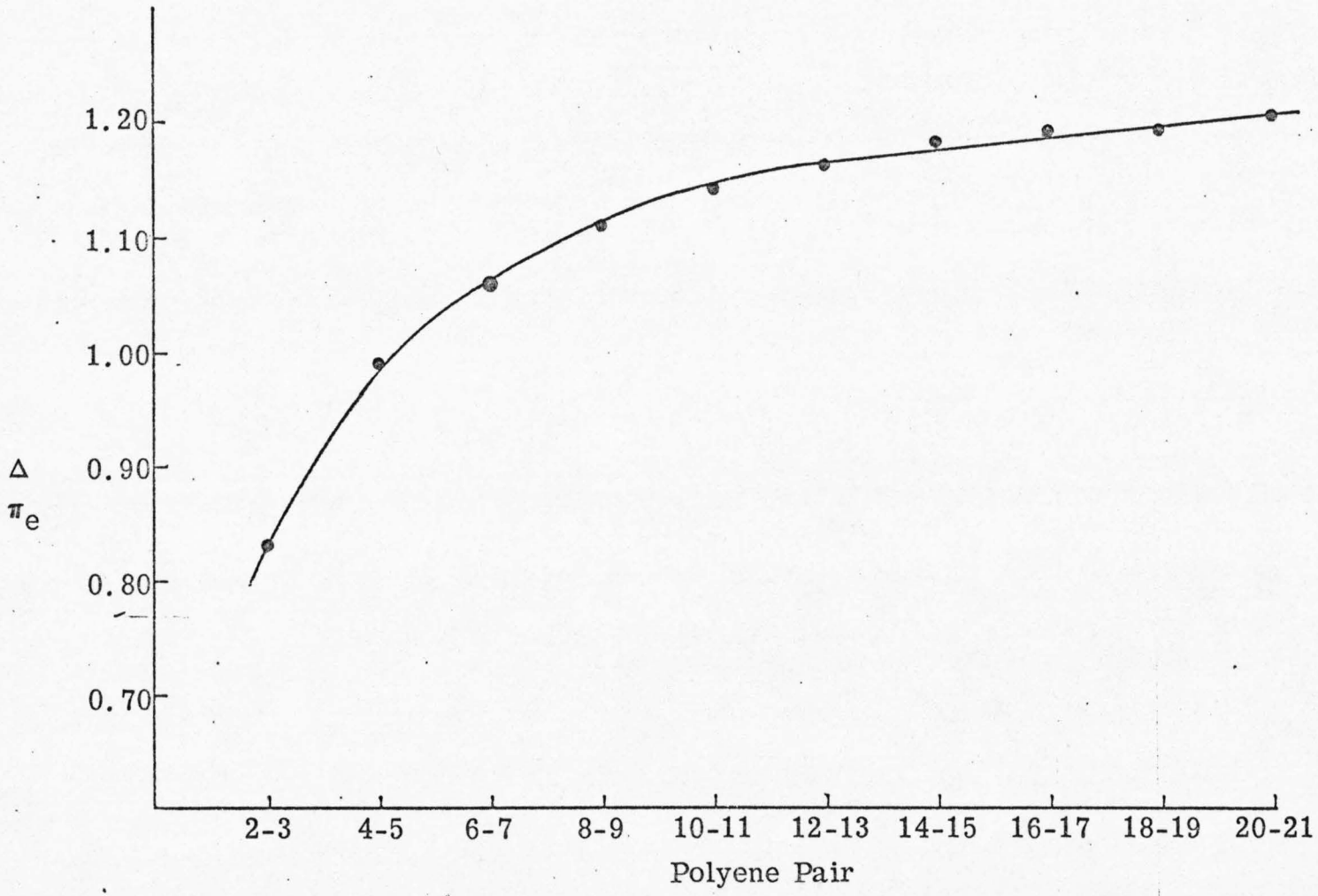
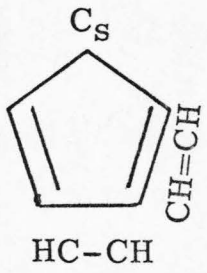


Figure 3. Change in π Energy vs. Polyene Pair for Linear Polyenes.

In propenyl ion, charge can only be found on primary carbon carbons. Intuitively then charged primary carbon (C_p) is assigned the additivity energy of 0.83 β. For tertiary charged carbon it is not possible to perform the same kind of analysis as for secondary carbon. However an additivity will be assumed among the different kinds of charged carbons and charged tertiary carbon (C_t) is assigned the additivity energy 1.60 β. In this method there is no difference in energy for positively or negatively charged carbons. This comes about because the linear polyene ions have the same π energy regardless of charge due to the presence of a nonbonding HMO in the set of orbitals for these molecules.

The calculation for cyclopentadienyl is given in Equation (3).



$$E = 2(CH{=}CH) + (HC{-}CH) + C_s = 5.81\,\beta$$

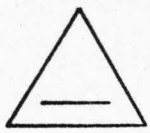
$$RE = E_{HMO} - E_{calc} \qquad (3)$$

$$\underline{\text{cation}} \quad RE = (5.23 - 5.81)\beta = -0.58\,\beta$$

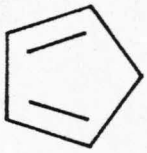
$$\underline{\text{anion}} \quad RE = (6.47 - 5.81)\beta = 0.66\,\beta$$

The calculations for a series of ions are listed in Table II. Where resonance forms with different kinds of bonds were possible for an ion, the average energy is listed.

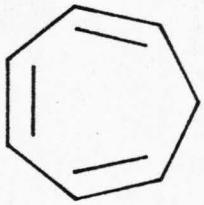
In interpreting the results of this method it is important to realize that the energy obtained by additivity represents the energy of the cyclic species in which there are only polyene-like interactions. The resonance energy as defined here represents stability due to the



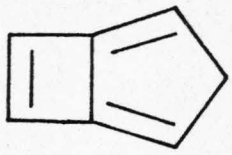
XX



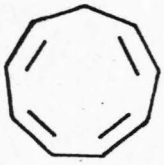
XXI



XXII



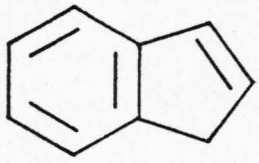
I



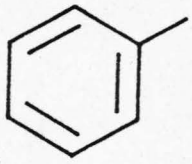
XXIII

n = 9

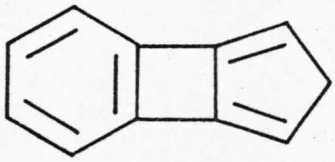
XXIV



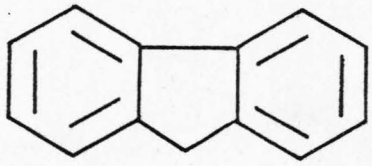
XXV



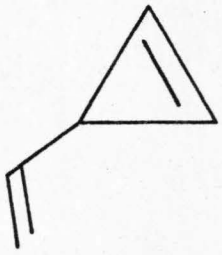
XXVI



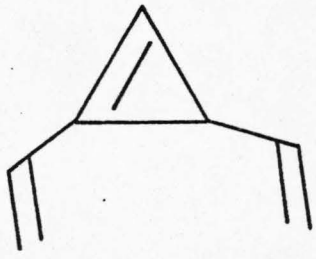
XXVII



XXVIII



XXIX



XXX

Structure of ions listed in Table II

Table II. Resonance Energies[a] of Cyclic Ions

Compound[d]	HMO[b] Pi Energy	Calc[c] Pi Energy	RE	REPE
XXa	4.00	3.27	0.73	0.36
XXb	2.00	3.27	-1.27	-0.32
XXIa	5.23	5.81	-0.58	-0.17
XXIb	6.47	5.81	0.66	0.11
XXIIa	8.99	8.35	0.64	0.11
XXIIb	8.07	8.35	-0.28	-0.035
Ia	8.92	8.80	0.12	0.020
Ib	8.92	8.80	0.12	0.015
XXIIIa	10.82	10.89	-0.07	-0.009
XXIIIb	11.52	10.89	0.63	0.063
XXIVa	26.46	26.08	0.38	0.019
XXIVb	26.76	26.08	0.68	0.031
XXVa	11.58	11.35	0.23	0.028
XXVb	12.17	11.35	0.81	0.081
XXVIa	8.72	8.33	0.39	0.065
XXVIb	8.72	8.33	0.39	0.049
XXVIIa	14.60	14.35	0.25	0.025
XXVIIb	15.03	14.35	0.68	0.056
XXVIIIa	17.54	16.89	0.65	0.054
XXVIIIb	17.91	16.89	1.02	0.073
XXIXa	6.43	5.77	0.76	0.19
XXIXb	5.35	5.77	-0.42	-0.070
XXXa	8.87	8.25	0.62	0.10
XXXb	7.98	8.25	-0.27	-0.034

[a] All energies in β.

[b] From ref. 3.

[c] From bond additivity.

[d] a $\equiv$ cation; b $\equiv$ anion.

cyclic structure over and above that due to simple polyene-like interaction. The fact that in some cases the resonance energy may be zero or even negative implies that the cyclic structure confers no extra stability to the system in question. It does not imply that the system cannot be synthesized or be incapable of isolation. Empirically, a correlation between stability and reactivity does exist, i. e., the less stable a substance is thermodynamically, the more reactive it usually becomes. Such a correlation however must be applied with caution to specific cases. For instance, most acetylenes have high heats of formation compared to other organic compounds yet they may be synthesized and isolated without problem.

In the case of cyclic ions it appears that the correlation of stability with reactivity can be applied because neutral precursors to these ions can usually find less energetic pathways open to them if the route to the ion is energetically unfavorable. Salts of the cyclopentadienyl anion (which is predicted to have a large positive resonance energy) are easily synthesized and isolated whereas the corresponding cation has never been isolated. Indeed, there is little evidence for even its transient existence (5). In general, predictions of stability for certain ions listed in Table II appear to be in accord with experiment. The systems of interest Ia and Ib are just slightly aromatic, in contrast to the predictions of the first method examined earlier.

CHAPTER II

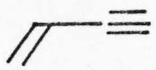
SYNTHESIS OF cis- AND trans-DIETHYNYLCYCLOPROPANE AND BICYCLO[3.2.0]HEPTA-1, 4, 6-TRIENE

Introduction

The synthesis of diethynylcyclopropanes presents two major difficulties. One is the need to incorporate into the same molecule two groups which are not easily prepared--the highly strained cyclopropane ring and the very reactive acetylenic triple bond. The other is to develop reaction conditions which minimize further transformations of these labile groups. In light of these difficulties, experiments were initiated with two general synthetic plans in mind differing in the timing of introduction of the acetylenic groups into the molecule.

The first plan consisted of two steps: (1) synthesis of a suitable cyclopropane precursor which contained the necessary acetylenic linkages and (2) preparation of the cyclopropane from this precursor. Since a general and well documented route to cyclopropanes is the addition of carbenes to olefins (25), an attractive precursor for step one would be an ethynyl substituted olefin such as XXXI or XXXII. Addition of methylene to XXXI or propargylene (XXXIII) to XXXII would yield the desired cyclopropane. The attractiveness of these reactions lies in the availability of the reactants and the relative mildness of the carbene additions.

XXXI



XXXII

$HC{\equiv}CCH:$

XXXIII

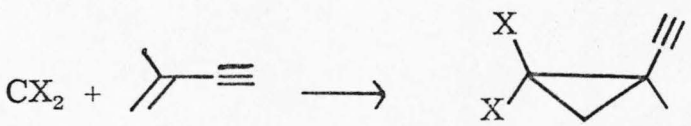
$H_2C{=}C{=}C:$

XXXIX

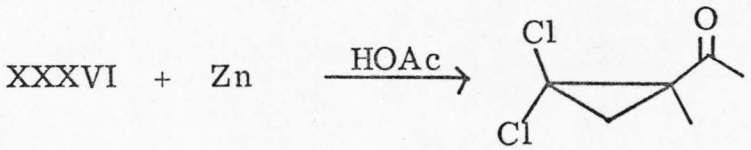
The second pathway is less attractive but more classical in approach. It requires the initial synthesis of a difunctional cyclopropane, the functionalities of which should be capable of easy conversion to acetylenic groups. An eliminative route to the acetylenes seems the most reasonable because of the many precedents in the literature (26) and because the cyclopropane ring is quite stable in basic environments. The major difficulty with this route is the requirement that a suitably difunctionalized cyclopropane be synthesized. However the desirability of introducing the reactive acetylenic linkages in the last step made investigation of this pathway worthwhile.

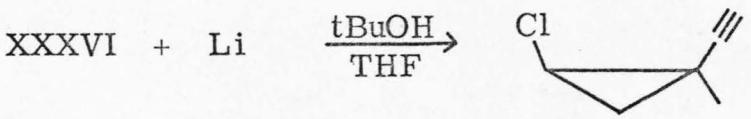
Results and Discussion

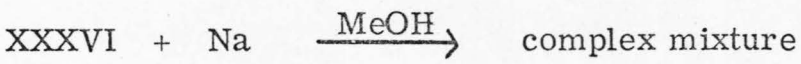
Carbene Addition Reactions. Initial studies were centered on the addition of dihalocarbenes to 2-methyl-1-buten-3-yne (XXXIV) (model system for XXXI) in the hope that 1,1-ethynylmethylcyclopropane (XXXV) could be obtained by reductive cleavage of the halogens from the initial adduct. The results are summarized below.

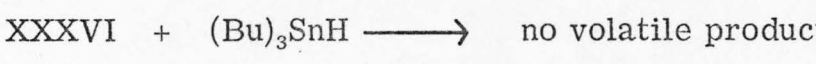


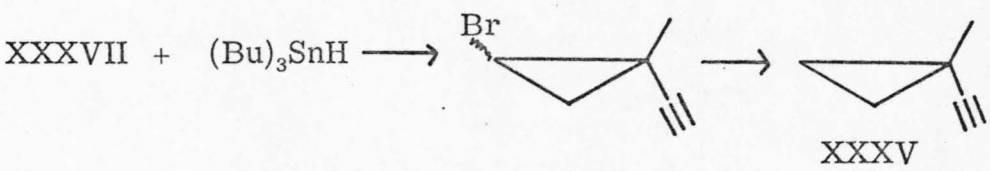
XXXIV XXXVI X = Cl
XXXVII X = Br









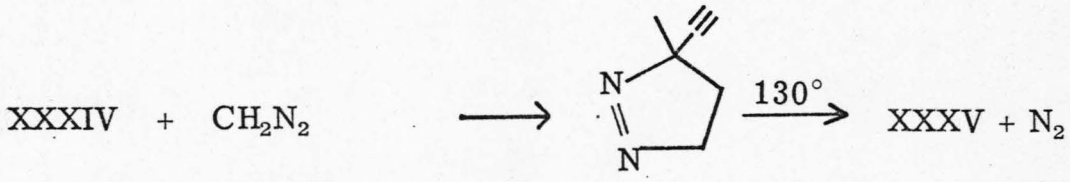


XXXV

Of the listed reactions only the last afforded XXXV. However the yield was not high enough to warrant further investigation. Probably the major cause of the low yield was addition of the tin hydride across the acetylenic triple bond. Dihalocarbene additions were not investigated further. Recent studies in our laboratories by R. Jones have shown that XXXI is inert towards a wide variety of carbene and carbenoid reagents.

A non-carbenoid method of introducing methylene is the pyrolytic decomposition of pyrazolines to cyclopropanes (27). Addition of diazomethane to XXXIV gave the expected mixture of

pyrazoline and pyrazole. Isolation and thermal decomposition of pyrazoline XXXVIII gave XXXV in moderate yields. Extension of this sequence to XXXI gave only a very complex unstable mixture on attempted preparation of the pyrazoline. Thermolysis of this mixture produced $<5\%$ of the expected amount of nitrogen.



XXXVIII

Work on the addition of methylene to XXXI having failed, reactions involving propargylene were investigated. Routes involving the addition of propargylene seemed desirable because all the starting materials were readily available and the above results indicated that carbenes could be added relatively easily to XXXIV.

Hartzler found that reaction of propargyl bromide, potassium t-butoxide and olefins produced products resulting from the addition of propargylene and allenylidene (XXXIX) to the olefin (28). These results gave promise of an easy, fast method for preparing propargylene. However attempts to repeat this reaction with XXXIV failed to produce any cyclopropane under a variety of conditions. The major isolable product was propargyl-t-butyl ether resulting from displacement of bromide by t-butoxide. When either methyllithium or lithium diethylamide were substituted for potassium t-butoxide only polymeric materials were isolated. The failure of these reactions may have

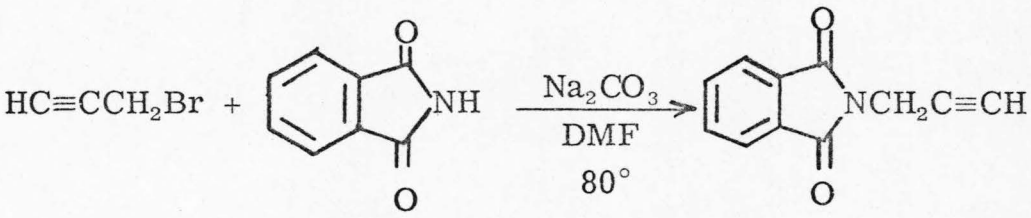
been due to the presence of the labile acetylenic hydrogen on XXXIV. Precipitation of the acetylenic salt might have precluded further reaction.

$$HC{\equiv}CCH_2Br + KO\text{-}\underline{t}\text{-}Bu + XXXIV \longrightarrow HC{\equiv}CCH_2O\text{-}\underline{t}\text{-}Bu$$

A more reliable precursor of propargylene is diazopropyne (XL). Skell found that photolysis of XL in the presence of olefins gave ethynylcyclopropanes (29). The addition is non-stereospecific lending support to the proposed triplet character of XXXIII. The preparation is fairly straightforward and is very close to that given by Gramas (30).

The yellow diazopropyne solution was stable at room temperature and reacted slowly with benzoic, p-nitrobenzoic and acetic acids. Only with trifluoroacetic acid was instant decolorization and nitrogen evolution noted. Diazopropyne was characterized by Ir analysis (bands at 3320, 2125, and 2075 cm^{-1}) and by reaction with dilute hydrochloric acid to give propargyl alcohol.

The photolysis of XL in the presence of XXXIV was investigated. Direct irradiation through a pyrex filter of a degassed mixture of XL, XXXIV and pentane in an evacuated sealed tube at -78° led to the disappearance of XL and the formation of three new products. Control experiments showed that these new products were the result of reaction of XL with XXXIV and not the reaction of either of these with itself. A preparative scale photolysis done in ether at 0° yielded sufficient material for analysis. Upon preparative gas



$$\xrightarrow[130^\circ]{\phi CH_2NH_2} HC{\equiv}CCH_2NH_2 \xrightarrow{HCl} HC{\equiv}CCH_2NH_3^+Cl^-$$

$$\xrightarrow[100^\circ]{KCNO,\ H_2O} HC{\equiv}CCH_2NHCONH_2$$

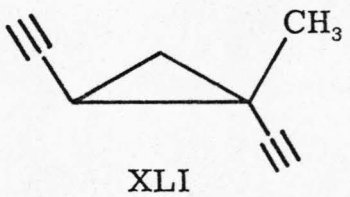
$$\xrightarrow[H_2SO_4]{NaNO_2} HC{\equiv}CCH_2N(NO)CONH_2$$
$$0^\circ$$

$$\xrightarrow[H_2O]{Na_2HPO_4} HC{\equiv}CCHN_2$$
$$0^\circ$$

XL

Scheme 1. Synthetic Route to Diazopropyne (XL).

liquid chromatography (glc) only one product was isolated in pure form. The other two products, observable by analytical glc, appeared to have decomposed upon preparative glc. The isolated material is assigned the formula XLI.



XLI

Mass spectral (ms) and elemental analysis data confirm the empirical formula C_7H_8. The presence of a terminal acetylene, cyclopropane ring, and methyl group was suggested by infrared (ir) absorptions at 3300, 2130 cm^{-1} (acetylene), 3090, 3010, 1055 cm^{-1} (cyclopropyl), and 2965, 2870, 1440, 1390 cm^{-1} (methyl). A nuclear magnetic resonance (nmr) spectrum taken at 220 MHz displays an AMX pattern for the cyclopropyl hydrogens. This pattern may be analyzed by first order methods.

Table III. Nmr Data for 1-Methyl-1,2-diethynylcyclopropane (XLI)

H		mult	J (Hz)
a	9.25	apparent triplet	6, 4.5
b	8.73	doublet of doublets	9, 4.5
c	8.58	singlet	
d	8.30	apparent triplet (finely split)	9, 6, 2
e	8.23	singlet	
f	8.18	doublet	2

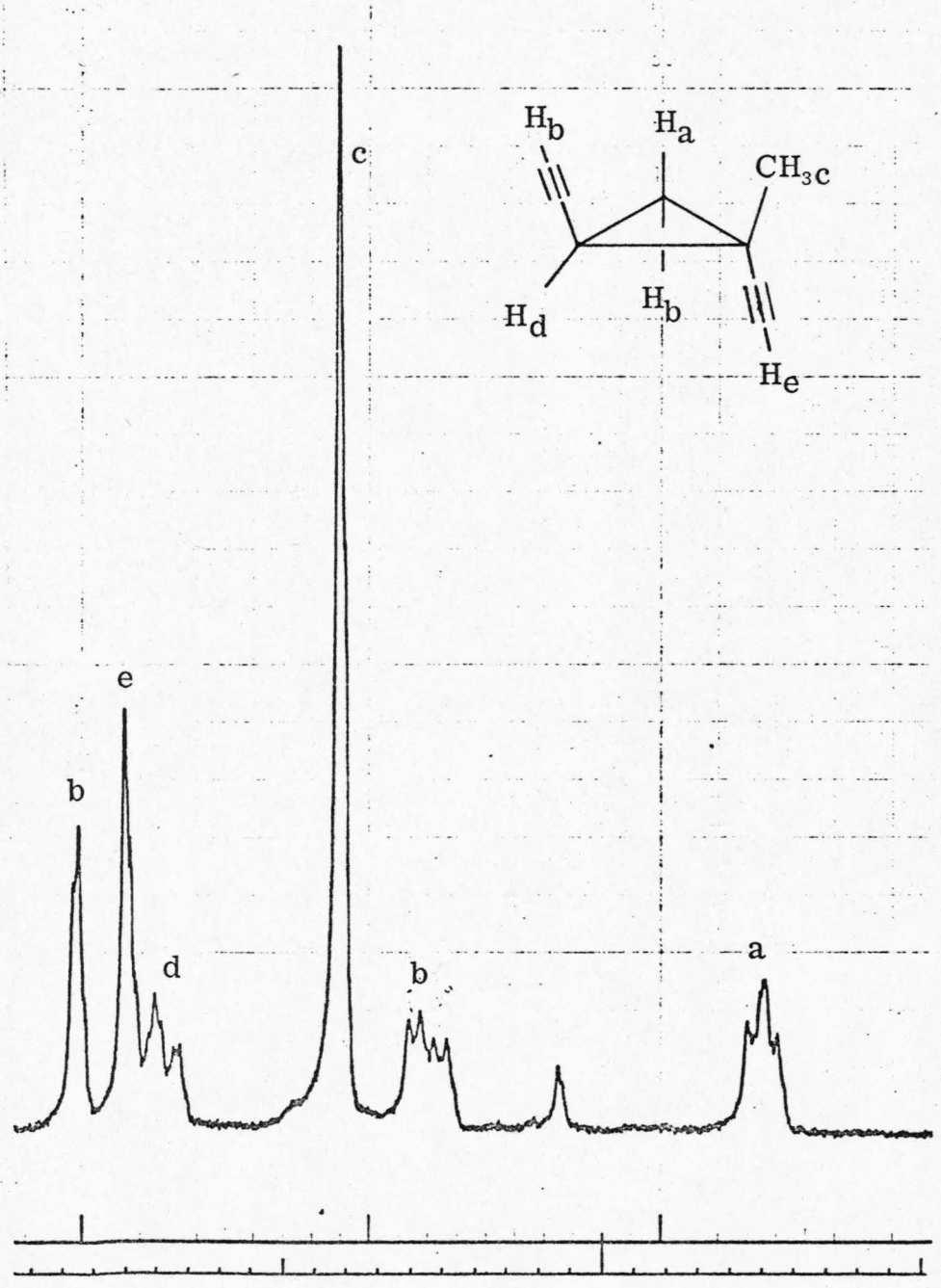


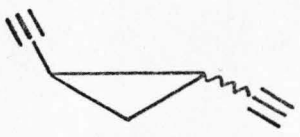
Figure 4. 220 MHz Nmr of 1-Methyl-1, 2-diethynyl-cyclopropane

Lacking a double resonance experiment it is not possible to definitely assign the coupling constants. However it is possible to reduce the possibilities of two sets:

	1	2
gem	$J_{ab} = -9$	$J_{ab} = -4.5$
trans	$J_{ad} = 4.5$	$J_{ad} = 6.0$
cis	$J_{bd} = 6.0$	$J_{bd} = 9.0$

The geminal coupling constant is assumed to be negative in accord with findings for other cyclopropanes of similar structure (31). Other possible sets where $J_{bd} > J_{ad}$ are ruled out because J_{cis} is always greater than or equal to J_{trans} for a given cyclopropane (31). Assignment of the stereochemical relationship of the acetylene groups is not possible from nmr data alone. The ethynyl groups are tentatively assigned the trans configuration because later experiments have shown that cis-diethynylcyclopropane is very unstable in neat form. Compound XLI is quite stable neat at room temperature.

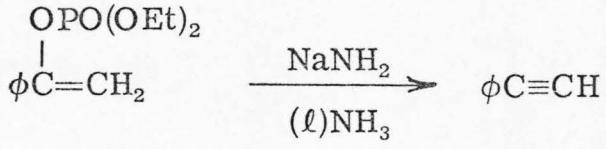
The Eliminative Route. cis and trans-Diethynylcyclopropanes. Theoretically it should be possible to prepare the unsubstituted diacetylene XVIII by the same route as XLI.

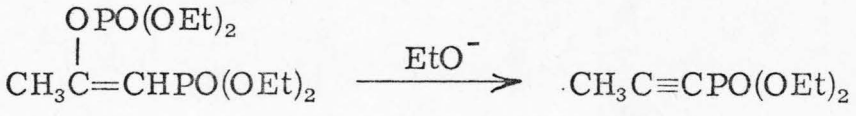


XVIII

Practically the difficulties in handling vinylacetylene and the low overall yield do not make such a route very attractive. It was decided to investigate routes in which an appropriate difunctional cyclopropane was converted to XVIII in the last step. Since acetylenes are most conveniently made by elimination reactions, synthesis of a cyclopropane capable of facile eliminative reaction to XVIII became the immediate synthetic goal.

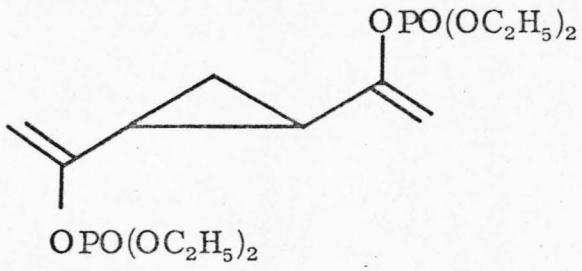
There have been several reports in the literature on the elimination of phosphoric acid derivatives from enol phosphates to give acetylenes. Cymerman-Craig found that substituted phenylacetylenes could be prepared by treating diethylvinyl phosphates with sodamide in liquid ammonia (32). Jacobsen noted a similar result in the reaction of XLII with sodium ethoxide (33).





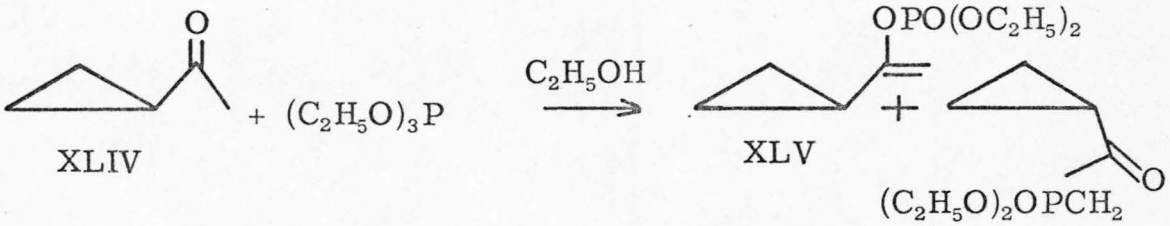
XLII

Extension of these results to the cyclopropyl system would require the preparation of the bis enolphosphate XLIII.



XLIII

Enol phosphates are usually prepared by the reaction of chloromethyl ketones with triethyl phosphite (34). Since at the time chloromethylcyclopropane was more easily available than the difunctional cyclopropane, it was decided to determine the feasibility of the phosphate eliminative route by working with the monofunctional cyclopropane. Chloromethylcyclopropylketone (XLIV) was prepared by the reaction of aqueous hydrochloric acid with the diazoketone obtained from the reaction of cyclopropylcarbonyl chloride with diazomethane (35). Reaction of XLIV with triethyl phosphite in ethanol or diglyme gave a 50:50 mixture of enol phosphate XLV and ketophosphonate XLVI.



XLIV XLV XLVI

Compounds XLV and XLVI were identified by the nmr spectrum of the mixture. Glc analysis showed the presence of only two peaks.

Compound	mult	$J_{P^{31}H}$ (Hz)
XLV	doublet of triplets [b]	2
XLVI	doublet [c]	22.5
$RC(OPO(OEt)_2)=CH_2$ [a]	doublet of triplets [b]	2
$RCOCH_2PO(OEt)_2$ [a]	doublet [c]	18

[a] R = P-$NO_2C_6H_5$, ref. 34.

[b] Refers to olefinic hydrogens.

[c] Refers to hydrogens α to p.

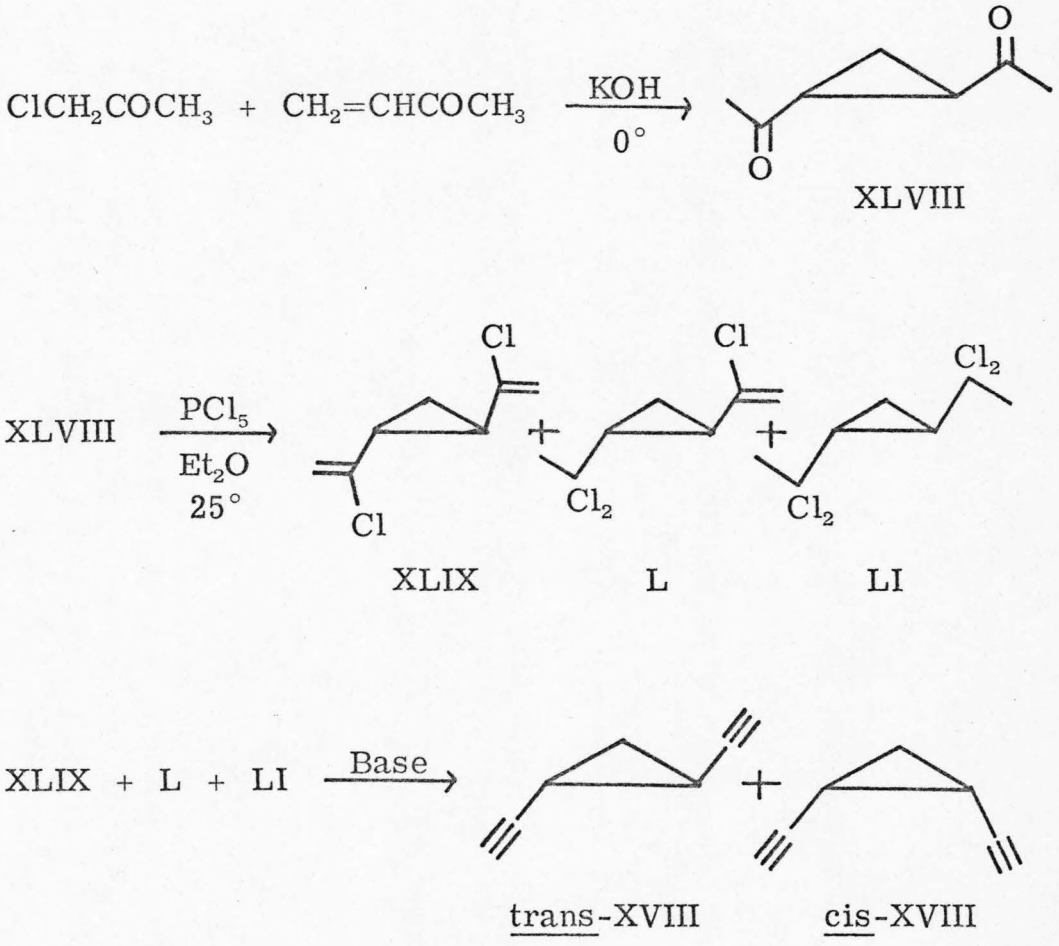
Attempts at base catalyzed elimination were performed on the mixture of XLV and XLVI. Bases used were potassium t-butoxide, sodamide, diazabicyclononene (DBN), lithium diisopropylamide and sodium ethoxide. Presence of cyclopropylacetylene (XLVII) was checked for by spiking the product mixtures with authentic cyclopropylacetylene prepared by the reaction of 1,1-iodocyclopropylethylene with potassium t-butoxide in dimethylsulfoxide (36). Although in most cases new volatile materials were formed, in no cases was XLVII detected. Since elimination to the acetylene could not be affected, this route was abandoned.

The more classical route for preparation of acetylenes is elimination of hydrogen halide from vinyl halides or two molecules of hydrogen halide from dichloroethanes. Jacobs and Pomerantz have considered in detail the preparation of acetylenes by this route (37).

In the present case an appropriately substituted bis-polychloroalkyl or alkenyl cyclopropane would serve as precursor to diacetylene XVIII. The successful preparation of the precursor and the diacetylene are outlined in Scheme 2. The condensation of chloroacetone with methylvinyl ketone finds precedent in the reaction of methyl acrylate with bromoethylacetate to give ethylmethylcyclopropane dicarboxylate (38). In the present reaction chloroacetone is condensed with methylvinyl ketone in the presence of potassium hydroxide pellets to give a 35% yield of trans-1, 2-diacetylcyclopropane (XLVIII). An attempt to improve the yield by substituting methanolic potassium hydroxide for the pellets resulted in recovery of only a small amount of XLVIII. The major product was 4-methoxybutan-2-one resulting from Michael addition of methoxide to methylvinyl ketone. The assignment of structure was strongly suggested by the simple nmr spectrum which consisted of two singlets at 7.91 and 6.78 τ and two triplets at 7.43 and 6.45 τ.

$$CH_2{=}CHCOCH_3 \quad + \quad CH_3OH \xrightarrow{KOH} CH_3OCH_2CH_2COCH_3$$

Substitution of water for methanol did not improve the yield of dione XLVIII but did result in the production of a significant amount of higher boiling hydroxylic material which was not characterized. The idea behind adding water and methanol was to provide better mixing between the base and reactants. Apparently this only enhances the formation of other products. The success of the reaction when using pellets may imply that the reaction is taking place on the



Scheme 2. Synthetic Route to cis and trans-Diethylnylcyclopropanes (XVIII).

surface of the pellets.

Spectral and elementary analysis data strongly suggested the assignment of structure for XLVIII. In the ir spectrum bands for the methyl hydrogen stretch at 2965 and 2915 cm^{-1} are very weak while the carbon carbon vibrations at 1425, 1360 and 1325 cm^{-1} are very strong. These results are consistent with the ir behavior of methyl ketones (39). The presence of a cyclopropyl group is confirmed by the presence of bands at 3000 and 1030 cm^{-1}. The major ketone band at 1700 cm^{-1}, shifted slightly to lower wavenumber relative to unconjugated ketones, is consistent with a carbonyl group conjugated to a cyclopropane (40). Nmr data and assignment of configuration will be discussed below.

Reaction of XLVIII with phosphorous pentachloride in ether at 25° gave the mixture of chlorides XLIX, L, LI in 45% yield. The time for completion of the reaction varied from run to run but the reaction could be followed conveniently by glc. About 30% of the product mixture were other products which were not characterized but are probably acyclic chlorides derived from ring opening of the cyclopropane ring. (Ring opening in the reaction of cyclopropyl ketones with phosphorous pentachloride was observed by Newman (41).) Attempts to prepare the vinyl chloride XLIX by reaction of XLVIII with triphenylphosphine dichloride were not successful (42).

The individual yields and analysis of the ir spectra for chlorides XLIX, L, LI are given in Table IV.

Table IV. Ir Spectral Data[a] for Chlorides XLIX, L, and LI

	Chloride		
Chloride	XLIX	L	LI
yield[b]	11.8	47.8	17.6
=C-H and ▷H stretch	3100 3020	3100 3005 2987	3005 2987
H_2C-H stretch	–	2937 2867	2937 2867
$C=CH_2$ stretch	1625	1625	–
△ stretch	993	993	993
=C-H bend	877	878	–
C-Cl stretch	700 670	705 670	707

[a] IR absorptions given in cm^{-1}.

[b] Relative yield based upon total product mixture.

Reaction of the entire chloride mixture with potassium t-butoxide in diglyme at 25° gave a mixture of cis and trans-diethynylcyclopropane in 15:85 ratio. Reaction in t-butanol gave only trans-XVIII. The yield from chlorides XLIX, L, LI is about 30% in both cases. Ready isomerization of trans-XVIII to a mixture of cis and trans-XVIII in diglyme but not in t-butanol was observed in control experiments. It appears that the equilibrium ratio in diglyme is 75:25 in favor of the trans compound. Attempts to increase the yield by varying solvent and temperature were not successful. Use of a

variety of other bases did not seem to help either. The chlorides were inert to sodamide in decane or mineral oil at elevated temperatures. Reaction did occur with sodamide in liquid ammonia but no XVIII was produced. Under a variety of conditions and solvents no XVIII or only a small amount of XVIII was produced by the reaction of the chlorides with sodium methoxide, potassium hydroxide, lithium diethylamide, sodium dimsylate, and sodamide-t-butanol. Elimination only to XLIX occurred with DBN while potassium 3-methyl-3-pentoxide gave XVIII in the same yield as potassium butoxide.

While trans-XVIII is a colorless liquid which is stable in air for extended periods of time, the cis isomer is extremely labile in the presence of oxygen even at -78°. Only dilution in solvent or storage in vacuo at low temperatures prevented the rapid polymerization of cis-XVIII. The empirical formula for trans-XVIII was confirmed by elemental analysis and by the presence of a parent peak in the mass spectrum at m/e 90. The cis isomer was too unstable for elemental analysis but glc-ms analysis showed the presence of a parent peak at m/e 90. The mass spectra of cis and trans-XVIII are almost exactly the same, confirming their isomeric nature. A summary of ir and mass spectral data for cis and trans-XVIII is given in Table V.

Assignment of Configuration. Configurational assignment of the ethynyl groups was made after examining the differences in the cyclopropyl ring proton absorption patterns in the 220 MHz spectra.

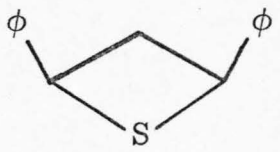
Table V. Infrared and Mass Spectral Data for trans and cis-Diethynylcyclopropanes

Ir	Absorption (cm^{-1}) trans-XVIII	cis-XVIII
C≡C–H stretch	3310	3310
▷-H stretch	3010	3010
C≡C	2140	2130
C≡C-H combinational	1220	1220
△ stretch	1060	1040
≡C–H bend	650	650

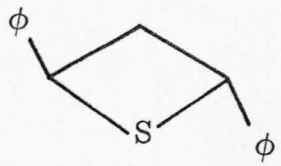
Ms[a] m/e	Ion	% Base Peak	
90	$C_7H_6^+$	16	14
89	$C_7H_5^+$	100	100
86	$C_7H_2^+$	4	3
63	$C_5H_3^+$	52	49
51	$C_4H_3^+$	32	24
39	$C_3H_3^+$	38	27

[a] At 70 ev electron energy.

By symmetry trans-XVIII contains only two chemically different types of ring protons while cis-XVIII bears three. Barring any accidental magnetic equivalences, this difference should be made evident in the 220 MHz nmr spectra. Relative chemical shifts here are increased by a factor of 3.5 compared to 60 MHz spectra. Examination of the spectra reproduced in Figures 5 and 6a in fact confirms these differences. Trans-XVIII displays two apparent triplets while cis-XVIII displays one four line pattern and two six line patterns. These assignments based upon the symmetry of the cyclopropane should be quite reliable. The same type of analysis was used to distinguish between cis and trans thietanes LII and LIII (43).



LII



LIII

The configuration of the precursor systems may be chemically correlated to trans-XVIII. Since under nonequilibration conditions only trans-XVIII is formed from the chlorides, it is reasonable to assume that the chlorides themselves possess the trans configuration. Likewise, assuming no cis-trans isomerization in the chlorination reaction, trans stereochemistry for the formation of diketone XLVIII is assumed.

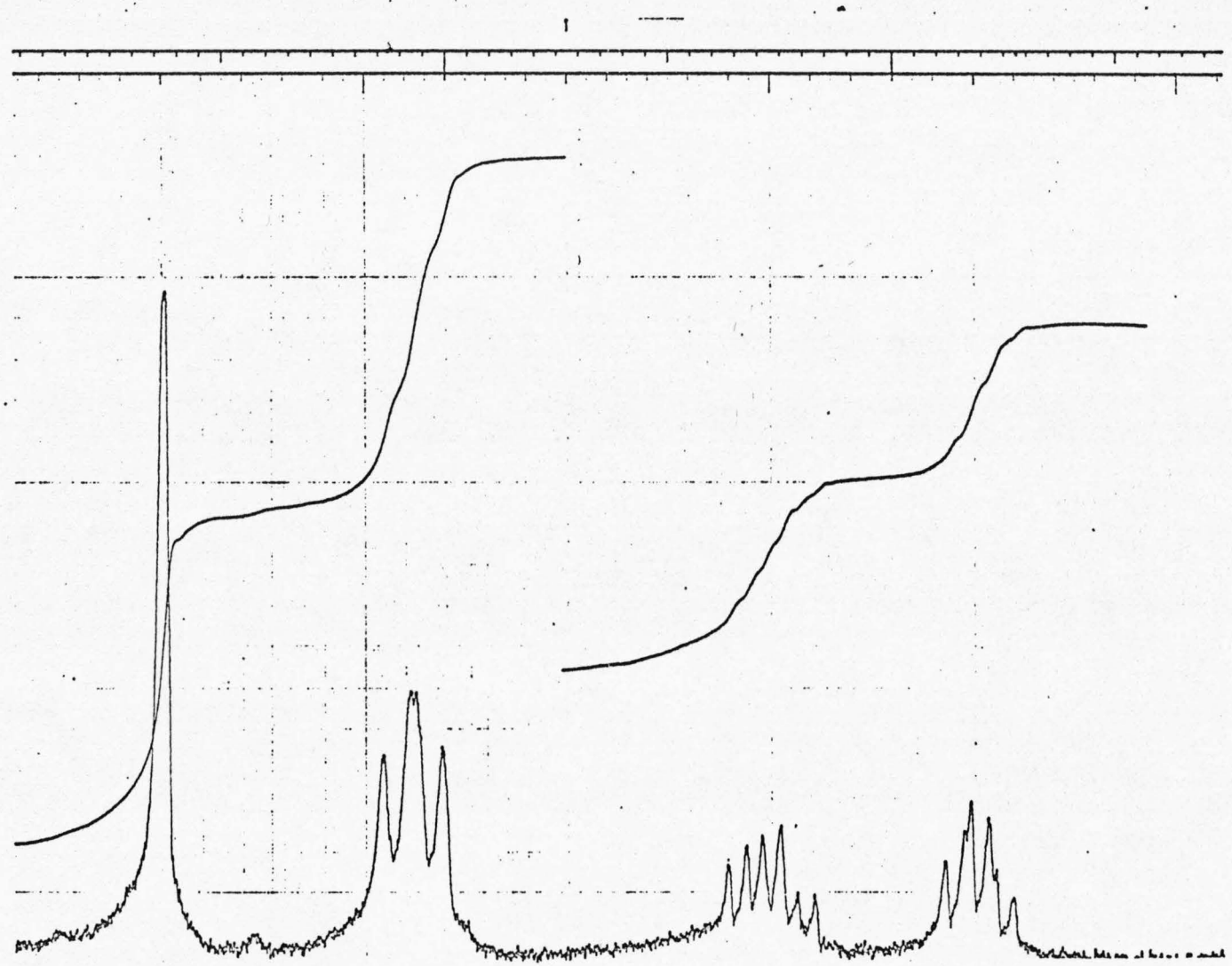


Figure 5. 220 MHz Nmr Spectrum of cis-1, 2-Diethynylcyclopropane in CCl_4

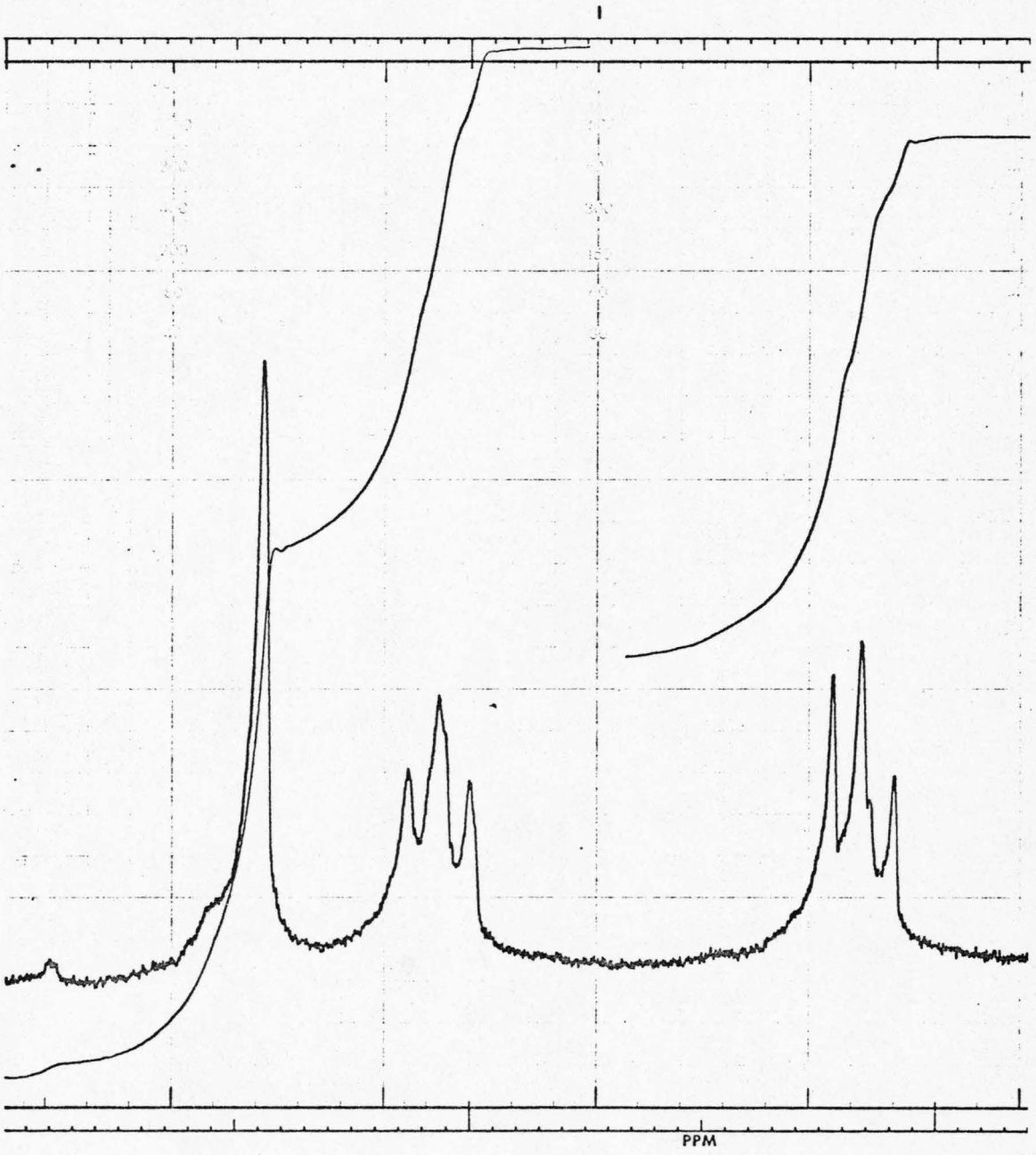


Figure 6a. 220 MHz Nmr Spectrum of trans-1, 2-Diethynylcyclopropane in CCl_4

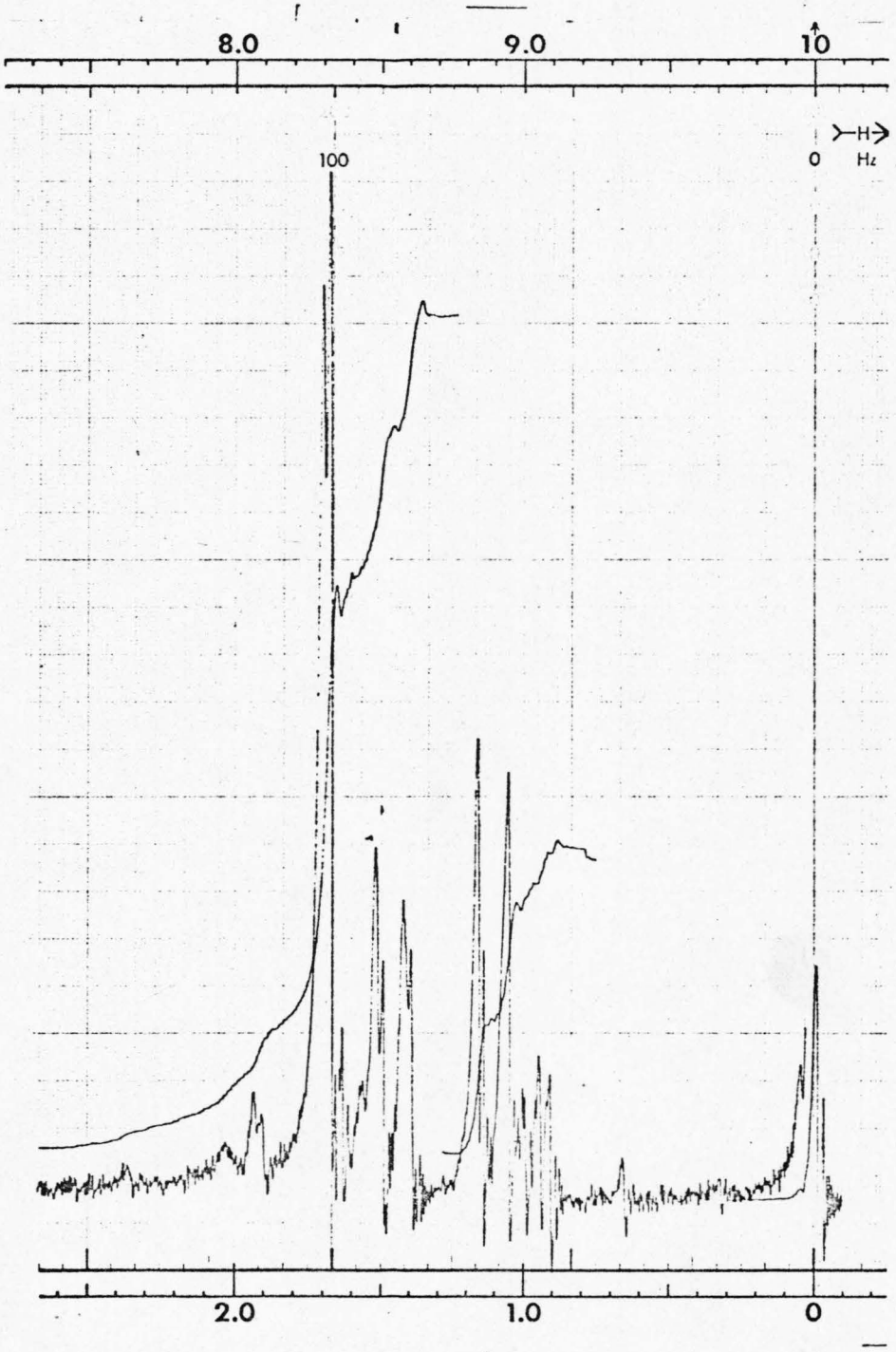


Figure 6b. 60 MHz Nmr Spectrum of trans-1, 2-Diethynylcyclopropane in CCl_4

Figure 7. Cyclopropyl Hydrogen Absorption Region in the 60 MHz Nmr Spectrum of XLIX in CCl_4

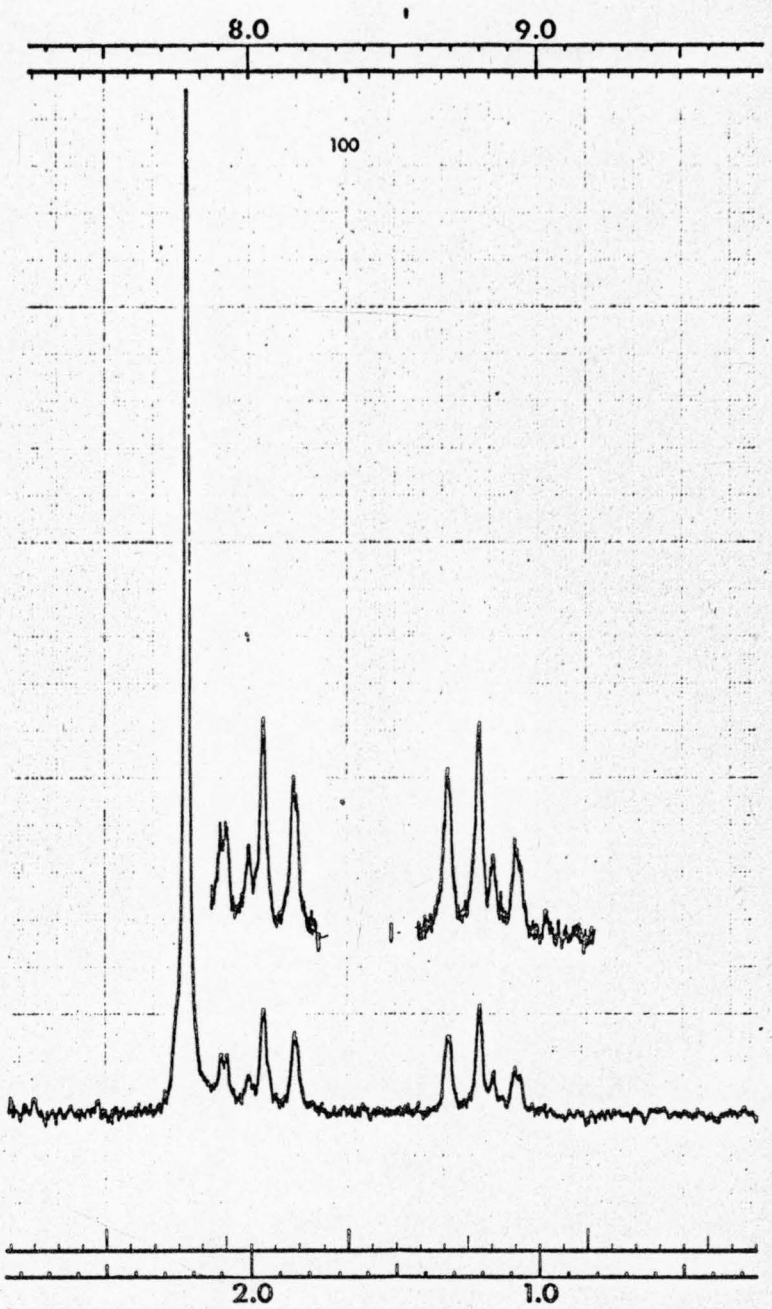


Figure 8. 60 MHz Nmr Spectrum of LI in CCl_4

Figure 9. 60 MHz Nmr Spectrum of trans-Diacetylcyclopropane in CCl_4

The configurations of the precursors may be assigned with more certainty by examination of their nmr spectra. As in trans-XVIII only two different groups of absorptions are expected for the trans-dichloride XLIX, trans-tetrachloride LI and diketone XLVIII. In fact, only two are observed (Figures 7, 8 and 9). For the unsymmetrically substituted trichloro compound L, no distinction can be made on grounds of symmetry because for either cis or trans all the protons are chemically nonequivalent. Assignment in this case must rely upon the chemical correlation.

Bicyclo[3.2.0]hepta-1, 4, 6-triene (I) and 2-Methylbicyclo-[3.2.0]hepta-1, 4, 6-triene (LIV). After the successful syntheses of diethynylcyclopropanes XVIII-t and XVIII-c, studies on their thermal behavior were initiated. Thermal rearrangements may be studied in the liquid or gas phase. Although the liquid phase may be more convenient for preparative scale reactions, these studies were confined to the gas phase for several reasons. Huntsman reported explosive decomposition when the rearrangement of XI was attempted in a sealed tube. Certainly the same behavior would be expected for acetylenes XVIII-t and XVIII-c. Also, since the hoped for product is highly strained, it might be quite labile in the condensed phase at elevated temperatures. The most practical reason is that for the temperature range used during initial studies ($>300°$) a gas phase system presented the least difficulties in assembly and use.

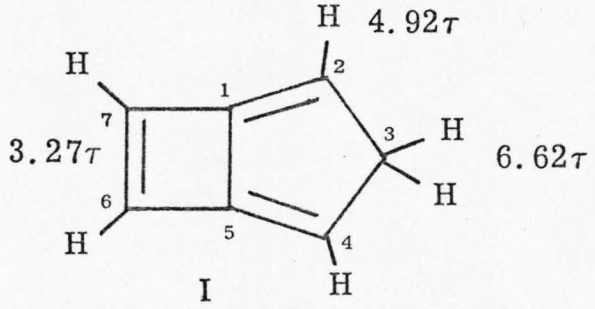
Two preparative gas phase systems were constructed: an atmospheric pressure flow unit and a high vacuum flow unit. Later a static system was employed for kinetic studies. Since initial work was with the atmospheric flow system these results will be described first.

The atmospheric flow unit consisted of an open tubular oven in which rested a Pyrex tube. One end of the tube was connected to a vaporization flask and the other to a cold trap. In a typical experiment, the diacetylene XVIII either neat or in an inert solvent was vaporized by a nitrogen flow through the heated portion of the tube (~20 cm) and the effluent condensed into a trap cooled by dry ice/acetone or by a carbon tetrachloride slush bath (-25°).

Pyrolysis at 350° of a 10% solution of XVIII-t in carbon tetrachloride gave a new material in 30-40% yield. Spectral and chemical evidence strongly suggested that the new substance was triene I. The empirical formula was confirmed by the appearance of a parent peak at m/e 90 in the mass spectrum. The simplicity of the infrared spectrum of I is indicative of the relatively high symmetry of the molecule. Absorption bands at 3100, 3075 and 2885 cm^{-1} are assigned to olefinic and methylenic carbon hydrogen stretches. The methylene carbon hydrogen stretch absorption is at relatively low frequency but this is apparently due to the presence of a five membered ring since the analogous stretch in cyclopentadiene is found in the same region. The rest of the triene spectrum is very simple showing weak olefinic stretches at 1600 cm^{-1} and a stronger

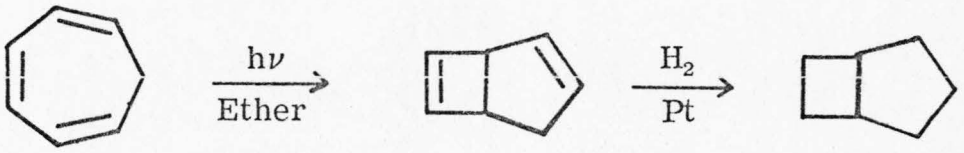
band at 935 cm^{-1}. The ultraviolet spectrum exhibited peaks at 204 (log ϵ = 4.0) and 272 (log ϵ = 3.0) nm. The analogous system XII absorbs at 211 and 248 nm (20).

An nmr spectrum of the pyrolysate exhibited three new resonances at 3.27, 4.92, and 6.62 τ. All resonances were finely split multiplets and integrated to the ratio 1:1:1. Comparison of this data with that for the model system XII points out the similarity in structures. Compound XII has resonances at 3.30, 5.32 and 5.43 τ, all very finely split. The nmr of I was analyzed as an $A_2M_2X_2$ system although there was some evidence of minor second order splitting. The coupling constants obtained from a first order analysis are J_{62} = 1 Hz, J_{63} = 1 Hz and J_{23} = 2 Hz.



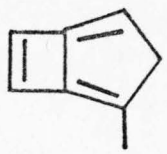
I

Confirmation of the bicyclic nature of I was obtained chemically. Hydrogenation of I in ethanol over a platinum catalyst gave a product whose ir spectrum was superimposable on the ir of bicyclo-[3.2.0]heptane, which was obtained from the reactions illustrated below



Triene I was isolated by preparative glc. It could be handled conveniently on a vacuum line except that it was adsorbed quite readily in Apiezon stopcock grease. Silicone grease did not present this problem. Isolated I is stable indefinitely in the liquid phase at -78° in vacuo or in the gas phase at 25°. The high reactivity of the substance is reflected in its instability to most other conditions. Storage neat in vacuo at 25° resulted in the slow deposition of a white solid which turned red with time. This reaction is a polymerization probably induced by acidic or basic sites in the glass. Reaction with oxygen is very facile. Even dilute solutions deposit a yellow polymeric material upon exposure to air, the half life of a 10% solution being about ten minutes. The polymer was insoluble in most solvents but did char in concentrated sulfuric acid. Although the composition of the polymer was not determined, it is probably a copolymer of oxygen with I, as is observed for XII (20).

The preparation of triene LIV was exactly analogous to that of I. The yields were about the same and the spectral data is given in Chapter VI.



LIV

The one drawback of the atmospheric pressure flow system was the low recovery of products. In addition to a significant amount of loss due to aerosol formation in the collector, a good portion of the total mass was converted to a brown polymeric coating on the walls of the Pyrex tube. The polymerization is most likely due to the relatively high concentration of reactive molecules during the course of the pyrolysis. Although variation of the oven temperature might have alleviated the polymerization problem it was decided to investigate the feasibility of a vacuum flow pyrolysis system. The advantage of the vacuum system is that reactions could be run at very low pressure, thereby inhibiting polymerization, and virtually quantitative trapping of volatile products could be realized.

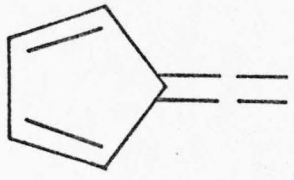
For a vacuum pyrolysis system the critical variables are pressure and temperature. At low pressure energy transfer from the hot walls to reactant molecules is inefficient because of the reduced number of wall-molecule and molecule-molecule collisions. The small residence time of a reactant molecule in the hot zone even further reduces the chance of a reactive collision. Thus under these conditions the observed extent of reaction is reduced relative to high pressure reactions at the same temperature. In order to compensate for this effect the temperature or the pressure of the system must be raised. Increasing the temperature increases the likelihood that collisions that do occur will be reactive. The increase in pressure brings about more effective energy distribution by increasing the number of molecule-molecule collisions. Ideally one could

optimize conditions for reaction by adjusting both of these variables. However in practice it was easier to raise the temperature while maintaining a constant initial pressure. The pressure, of course, will change as the reactant distills through the hot tube. No attempts were made to measure the pressure fluctuations during the course of the vacuum transfer.

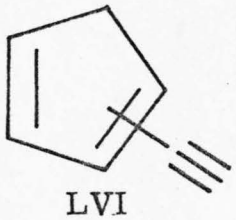
The atmospheric system was easily adapted for use as a vacuum flow system by fitting it with a connection to a vacuum pump, vacuum stopcocks, and a separate line for degassing samples. The procedure for pyrolysis was very simple. After degassing the sample by a freeze-thaw cycle, the collection flask was cooled in liquid nitrogen, the system closed to the vacuum pump, and the sample warmed and allowed to transfer through the hot tube into the collection flask.

Initial experiments on the vacuum flow pyrolysis of trans-XVIII gave very irreproducible results. Conditioning the glass walls by repeated passes of trans-XVIII improved reproducibility from run to run but did not suffice for day to day operation. Since quartz is less surface active than Pyrex, a quartz tube was employed. Immediately reproducibility was achieved even without prior conditioning. A study of the extent of reaction of trans-XVIII vs. temperature at initial pressure of 10 microns showed that reaction began at 380° and was complete at 480°. The cis-diacetylene XVIII reacted completely at 380°. The difference in reactivity between cis and trans-XVIII will be discussed in Chapter V.

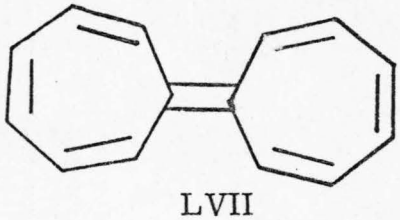
When trans-XVIII was pyrolyzed neat two new products other than I were observed. This is in marked contrast to the atmospheric system in which I is the sole product. The relative proportions of triene I and the new products was found to vary drastically with temperature and pressure. Increases in temperature and decreases in pressure favored the formation of the new products. Dilution of the reactant acetylene with hexane resulted in increased formation of I. In preparative scale reactions a third new product was detected. The identities of these new compounds are fulvenallene (LV), ethynylcyclopentadiene (LVI) and heptafulvalene (LVII). Their characterization and the temperature and pressure dependence of their formation will be discussed in detail in Chapter V.



LV



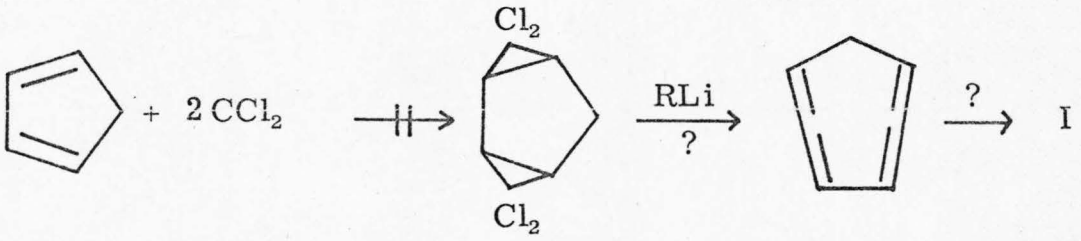
LVI



LVII

The new products did not pose a problem once conditions were adjusted to minimize their formation. Under these conditions (oven at 480°; initial pressure at 10-20 microns; 50/1 ratio of hexane to trans-XVIII), triene I constituted 80-85% of the product mixture. The triene could be easily separated from the remaining 15-20% by preparative glc. The actual yield of I was 50-70%. Triene LIV was prepared only by the atmospheric flow method.

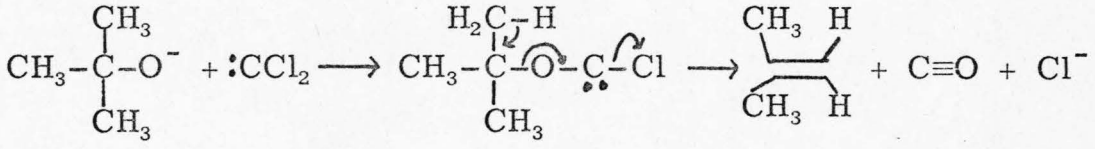
6-Chlorofulvene. At the outset of the present research, another method for preparing triene I was considered. Since the diallene LXI may be a transitory intermediate in the formation of I by the thermal route, synthesis of it might afford another route to I. Taking advantage of the synthesis of allenes by reaction of dihalocyclopropanes with alkyllithiums (44) a possible sequence is outlined below. An attempt to elaborate this scheme by preparing the diadduct LVIII failed but did result in the isolation of the previously unknown 6-chlorofulvene (LIX).



LVIII LXI

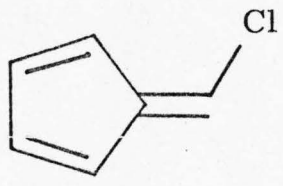
Reaction of cyclopentadiene, chloroform and potassium t-butoxide gave after workup and distillation an orange volatile oil. Glc analysis showed the oil to contain three components in a 2:1:5 ratio. Analysis of spectral data suggested that the first components were chlorobenzene and 1, 1-dimethyl-2, 2-dichlorocyclopropane (LX). The nmr of LX was very simple showing only two singlets at 8.63 and 8.82 τ in 3:1 ratio; the ir exhibited mainly aliphatic absorptions. Another worker in these laboratories (M. Sekera) has isolated the dibromo analog from the reaction of bromoform with potassium t-butoxide and allene. These compounds are apparently formed by the addition of the dihalocarbene to isobutylene, which can only be formed

by dehydration of t-butanol. Similar results have been reported for the neopentyl system (45). Based upon those results a possible mechanism for the formation of isobutylene is given below.



Chlorobenzene was never isolated but was identified from the presence of a broad singlet at 2.74 τ in the nmr of the product mixture. Also, addition of authentic chlorobenzene to this mixture gave only one glc peak at the retention time previously assigned to it.

The structure of 6-chlorofulvene was assigned to the major component after consideration of its spectral and chemical behavior. The uv, ir and color of the pure compound are consistent with those of fulvenes. The uv absorptions at 261, 263, 277 and 371 nm are shifted to longer wavelengths relative to fulvene itself. Similar shifts have been correlated with electron donating substituents in the six position of fulvenes. For instance, 6-acetoxyfulvene absorbs at 266, 273 and 361 nm (46). That chlorine can donate electrons by resonance is well established and it would seem to fall in line with these other systems.

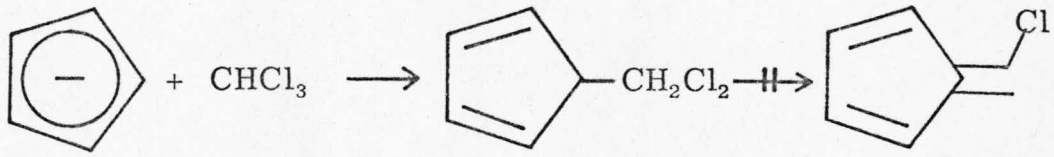


LIX

The nmr spectrum exhibited only olefinic absorptions at 3.22, 3.42-3.70 and 3.82-4.0 τ. These chemical shifts are in agreement with those of other fulvenes (46).

The final proof of structure is the isolation of 6-piperidinyl fulvene and piperidinyl hydrochloride from the reaction of LIX with neat piperidine. The mp and uv of the 6-piperidinylfulvene agreed well with literature values (47).

An attempt to prepare LIX by reaction of sodium cyclopentadienide with chloroform in THF at -20° was unsuccessful, neither LIX nor chlorobenzene being formed. This is somewhat surprising considering some recently reported related observations. Ter Borg reported isolation of chlorobenzene from the reaction of sodium cyclopentadienide and cyclopentadiene with chloroform (48). He reported no LIX although his workup conditions were quite drastic (nitric acid washes) and possibly LIX did not survive. Neuenschwander reported synthesis of substituted fulvenes in very good yield from the reaction of acetoxychloromethanes with sodium cyclopentadienide (49). The conditions were quite similar to the chlorofulvene reaction except that triethylamine was used to catalyze the elimination of acetic acid to give the fulvene. Perhaps cyclopentadienide could not catalyze elimination of HCl from the intermediate chloromethyl cyclopentadienide.



Parham has studied reactions similar to those reported above. He found that addition of dichlorocarbene to indene gave a monoadduct which underwent base catalyzed elimination to chloronaphthalene (50). However his attempt to extend the reaction to cyclopentadiene was unsuccessful--only dicyclopentadiene was isolated. Chlorobenzene has been prepared from cyclopentadiene and chloroform in gas phase reactions above 400° (51). Apparently dichlorocarbene is a reactive intermediate since reaction of deuterochloroform with cyclopentadiene gave only 0.5% deuterochlorobenzene. m-Chloropyridine may be prepared from pyrrole and chloroform by a gas phase reaction (52) or by reaction of the N-lithium salt of pyrrole with chloroform (53). No fulvenes were reported in any of the above reactions.

CHAPTER III

THE BICYCLOHEPTATRIENYL ANION

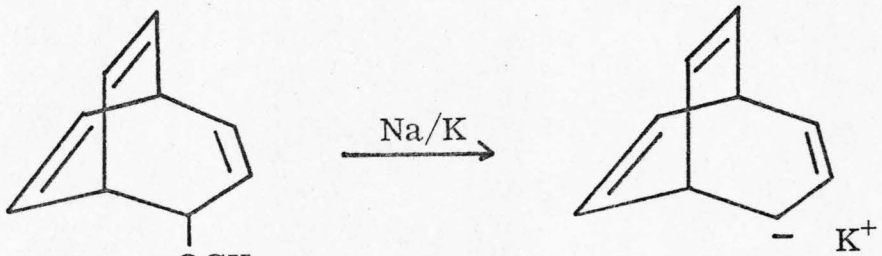
Introduction

The kinetic and thermodynamic acidities of hydrocarbons have been subjects of much study (54). Of the various compilations of acidities perhaps the most useful is the MSAD scale given by Cram (55). This scale shows quite well how such factors as charge delocalization, hybridization and aromaticity may affect hydrocarbon acidities.

We were concerned with the possibility that the bicyclic anion Ia might be aromatic. One way to assess this property would be to compare the acidity (pK_a) of I with that of cyclopentadiene (precursor to the aromatic cyclopentadienide system) and with that of cycloheptatriene (56) (precursor to the nonaromatic cycloheptatrienide system) (57). This comparison is especially interesting because the bicyclic system I may be considered as an ethylene fused to a cyclopentadiene ring. Breslow found that the interaction of the double bond decreases the acidity of the cyclopentadiene moiety by 10 pK_a units. This corresponds to 15 kcal/mole destabilization. If Breslow is correct the same results should be obtained starting from triene I.

Another reason for studying the generation of Ia from I is to check Breslow's claim that reprotonation of Ia takes place solely at the bridgehead position (17).

The preparation of anions can be achieved by several general methods. One of the most attractive because of its mildness is the alkali metal cleavage of aliphatic ethers and halides. Winstein (58) has found good success in this method as exemplified by the conversion of LXII to LXIII.



LXII LXIII

In the present study however ether and halide derivatives of triene I were not available. It was necessary to use methods by which the anion would be generated from the parent triene I. An obvious method is proton abstraction by a strong base. There are many literature precedents for this route and it does have the advantage of simplicity. However the main drawback in the present case is that the highly strained triene I might be prone to anionic polymerization under strongly basic conditions. This problem might be alleviated by running the reactions under dilute conditions, but initially the goal was to produce anion Ia in the relatively high concentrations needed for nmr spectral observation. Therefore most of the experiments described below were performed with this goal in mind.

Results

Reaction with Potassium t-butoxide. The use of potassium t-butoxide was suggested by Breslow's preparation of the anion Ia from the reaction of triene II with this base in DMSO (17). It was realized that reaction in DMSO-d_6 would not produce observable concentrations of the anion Ia since Breslow observed reprotonation to be fast in this medium. However what was hoped for was to observe deuterium exchange with the hydrogens in the methylene position of the triene. In addition to giving proof for the transient existence of anion Ia, under ideal conditions it might be possible to measure the rate of deuterium-hydrogen exchange. Comparison of this rate with rates of exchange obtained for such analogs as 1, 4-pentadiene, cyclopentadiene, and cycloheptatriene would be of great value in determining the effect of the bicyclic structure on the acidity of triene I.

The actual experiment consisted of observing the nmr spectrum of the triene in DMSO-d_6 as aliquots of a solution of one equivalent of potassium t-butoxide in DMSO-d_6 were added. The initial additions caused the immediate appearance of a black color and a decrease in the intensity of the triene absorptions. At the end of the addition the triene peaks had disappeared. At no time did it appear that the methylene absorptions decreased faster than the olefinic absorptions. This indicates that deuterium-hydrogen exchange was not observed in this experiment. However very weak new absorptions having the same chemical shift and peak shapes as dimers III and IV did appear.

Also, it appears from the spectrum that deuterium had been incorporated in the same positions of the dimers as reported by Breslow. The identity of the dimers was more definitely substantiated by comparison of their infrared spectrum with that supplied by Professor P. Radlick of University of California at Riverside.

The yield of the dimers was less than 5%. The rest of the mass was probably accounted for by polymer. By the end of the reaction the mixture was pitch black and small bits of black solid were discernible. The ease of the polymerization reaction was quite discouraging but it was hoped that in this case it was just a property of the t-butoxide-DMSO system and other systems might not exhibit such behavior. In addition, since formation of the dimers implied that at least some anion had been formed it was hoped that use of an aprotic solvent such as tetrahydrofuran (THF) and a base whose conjugate acid was very weak would decrease dimer formation from reprotonation and increase chances of observing anion Ia. Subsequent experiments were designed to test this supposition.

Reaction with Alkyl Lithiums. A number of experiments were performed employing n-butyllithium or triphenylmethyllithium as proton abstractors. These experiments and the respective reaction conditions are summarized in Table VI.

The procedure of Bates for the preparation of pentadienyl (59) and heptatrienyl (60) anions is both simple and successful. It consists of adding n-butyllithium in hexane to a mixture of the hydrocarbon and

Table VI. Alkyllithium Experiments[a]

Run	Reactants	Solvent	Temperature	Atmosphere
A	1, 4-pentadiene, NBL	THF, Hexane	-78° to 25°	Argon
B	Triene I, NBL	" "	" "	"
C	" "	" "	25°	"
D	" "	" "	-70° to 0°	"
E	" "	" "	-78° to 25°	"
F	" "	" "	" "	in vacuo
G	" "	Pentane	25°	Argon
H	" "	TMEDA	-40°	in vacuo
I	Triene, TML	THF	25°	in vacuo

[a] NBL ≡ n-butyllithium; THF ≡ tetrahydrofuran; TMEDA ≡ tetramethylethylenediamine; TML ≡ triphenylmethyllithium.

THF at -78°. After allowing the mixture to warm to room temperature an nmr spectrum of the anion may be obtained. Run A is a repeat of this procedure for 1, 4-pentadiene; Bates' results were reproduced exactly. Encouraged by this result the same reaction was attempted with triene I and n-butyllithium. Unfortunately, the results of reaction B were quite negative; an nmr of the mixture at 35° showed no new peaks which could not be accounted for by the THF-n-butyllithium combination. Moreover, no peaks due to triene I were present. This simple experiment having failed, it was decided to try the same reaction but at different temperatures, in order to ascertain if anion Ia could be produced only in a certain temperature

range. The temperature of reaction C was maintained at 25° throughout. Again, destruction of triene I was the only observable reaction. A variable temperature nmr experiment (D) showed no new absorptions at -70°, -50°, -30°, -10° and 0°. No peaks due to triene I were present. In all of the above nmr experiments the only isolable product was a yellow to brown highly insoluble polymer.

The possibility existed that the anion might be present in the above experiments but that its concentration was too low to be detectable by nmr spectroscopy. Accordingly, in the following set of experiments the presence or absence of dimers III and IV was checked for by glc after quenching with water or methanol. Detection of the dimers would be indicative of anion formation. After reaction E was quenched with water at -78° glc analysis showed no trace of the dimers or of triene I. This reaction underwent some vivid color changes, going from bright yellow at -78° to dark red at 25° and yellow again after the quench. The only detectable product was polymer. Reaction F run in vacuo gave the same results--no products other than polymer. Apparently oxygen was not the cause of polymerization because the reactants were thoroughly degassed before mixing. In an attempt to remove anion Ia as its lithium salt from the mixture as soon as it was formed, pentane was substituted for THF. The insolubility of the ionic salt might preclude further reaction. Analysis of reaction G however showed no dimers or triene I.

Next we attempted to favor anion formation by modifying the character of the base. It was reasoned that if polymerization was being enhanced in some way by the covalent character of the carbon-lithium bond in n-butyllithium, then conditions which favored ionization of this bond might also favor formation of anion Ia. It is known that tetramethylethylenediamine polarizes the carbon-lithium bond in n-butyllithium by complexing the lithium (61). Use of this substance as solvent in reaction H did not give the anion. Again, only polymer was isolated. Although the mechanism of this efficient polymerization is unknown it was reasoned that if the chain initiation step was addition of the base to triene I then use of a highly sterically hindered base might lessen the extent of polymerization. However the results of reaction I in which the bulky triphenylmethyllithium was the base were just as disappointing as the previous ones. No dimers were detected. No further attempts with alkyllithiums were made.

Reactions with Alkali Metals. The facile preparation of potassium cyclopentadienide from the reaction of potassium with cyclopentadiene led us to consider this reaction as a means of preparing anion Ia (62). It would have the advantage of mildness as in the Winstein reaction and the aprotic conditions involved would inhibit dimer formation.

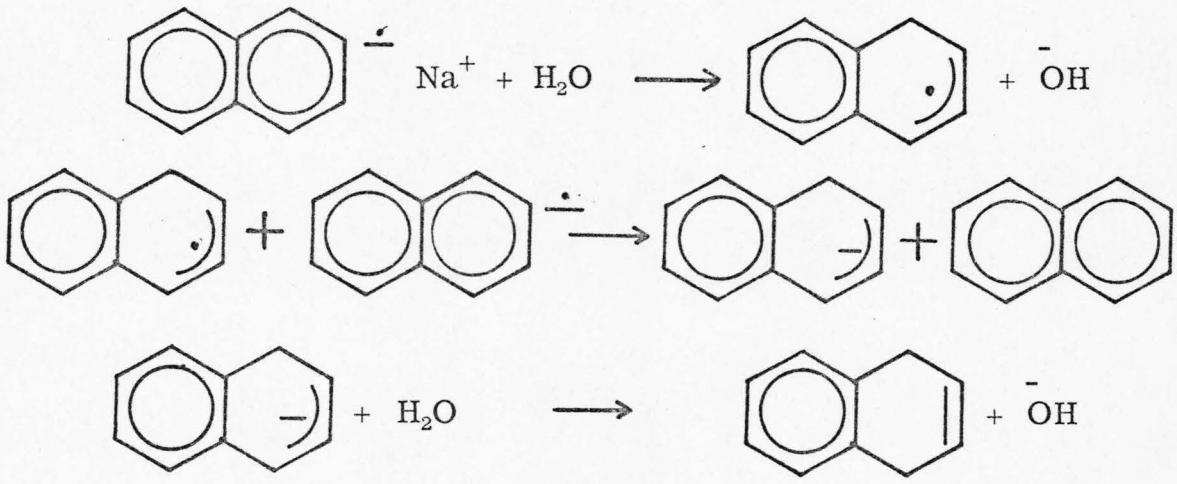
The reaction of potassium metal with triene I in THF at 25° under argon gave after one hour a 50:50 mixture of triene I and dimers III and IV. A similar experiment done in vacuo and utilizing a potassium mirror to enhance reaction gave a product mixture

consisting of ~80% dimers. Finally, a reaction in vacuo with sodium/potassium alloy gave all dimers. All of the above reaction products were detected by both nmr and glc. The yield of polymers in these reactions was much less than that obtained in the alkyllithium experiments.

The only reasonable source of protons in the above reactions was the triene itself. In order to cut down this presumed self exchange it would be necessary to run the reactions at high dilution of triene I. Although this kind of reaction was not performed for the alkali metals, an experiment designed to test this idea will be described later.

$$\text{I} + \text{K} \xrightarrow[25^\circ]{\text{THF}} \text{III} + \text{IV}.$$

Reaction with Naphthalene Radical Anion. The reaction of conjugated aliphatic hydrocarbons with radical anions has been the subject of only a few reports in the literature. Eisch (63) has reported the reaction of lithium biphenylide with triphenylmethane to give lithium triphenylmethide in greater than 90% yield. If application of a similar reaction to the present case were successful, a very attractive route to anion Ia would be at hand. The mechanism of the reaction of aromatic radical anions with water has been studied in detail and is presented below (64). An acidic hydrocarbon would be expected to be subject to the same reactions as water, assuming no competing reactions take place. The products of the reaction would



be the hydrocarbon anion, naphthalene and dihydronaphthalene. Admittedly this route would fail for hydrocarbon acids weaker than dihydronaphthalene. However, Bank (64) has estimated the pK_a of this species to be 35 which is well above the value reported by Breslow for triene II (9).

Naphthalene radical anion was prepared simply by stirring together naphthalene and sodium in dry THF. The solution which results from this electron transfer reaction is dark green in color and is stable for a period of hours in the absence of air and moisture. Reaction of cyclopentadiene with the radical anion was investigated as a model system. One equivalent of cyclopentadiene was added to a stirred solution of the radical anion. A mild exothermic reaction and immediate loss of the dark green color took place. The resultant mixture was water white. Treatment with water and extraction with pentane afforded the organic products. Analysis by nmr showed the

non-volatile products to be a nearly 50:50 mixture of naphthalene and dihydronaphthalene. Observation of the reaction products in this ratio implies that mechanism mentioned above holds for cyclopentadiene and that the cyclopentadienyl anion was formed. Cyclopentadiene was not checked for upon analysis of the products.

The same reaction with 1, 4-pentadiene, a much weaker acid, was more complex. The rate of the reaction was quite slow; the color changed from dark green to brown and finally to red. The reaction was quenched with D_2O at this point, causing the mixture to turn colorless. Analysis of the products showed less than 5% dihydronaphthalene, the bulk of the products being naphthalene. It would appear from the lack of the dihydro compound that no proton transfer took place between the radical anion and 1, 4-pentadiene. The good recovery of naphthalene implies that the main reaction was electron transfer to 1, 4-pentadiene. The products of this reaction were not investigated.

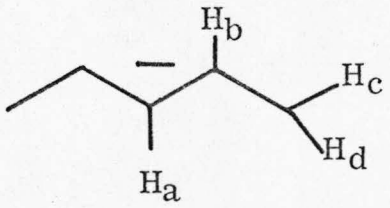
Addition of cycloheptatriene to sodium naphthalide caused an immediate color change from green to a very intense dark blue. An nmr of this blue solution exhibited much peak broadening. Besides solvent peaks only very broadened absorptions for naphthalene were present. This behavior may have been due to the viscosity of the solution but more likely was caused by the presence of a paramagnetic species. Addition of D_2O to the blue solution caused a change in color to orange. Naphthalene was the main product of the quench; neither dihydronaphthalene nor cycloheptatriene was detected by nmr analysis.

A good deal of polymer was isolated as a precipitate. Again, it appears that electron transfer to cycloheptatriene was the main reaction.

The reaction of triene I with the radical anion gave much the same results as cycloheptatriene except that there was no dramatic color change. A good yield of polymer (80% based on triene I) was isolated. The above reactions did not produce the desired results but deserve more detailed investigation.

Reaction with Amide Bases. As part of the continuing search for bases which might give the desired anion without the attendant polymerization the strong amide bases were tried. The first experiments were performed with potassium amide in liquid ammonia. Kloosterziel has obtained very good results in preparing and characterizing linear polyenic anions in this medium (65). However prior to knowledge of his results the reaction of 1, 4-pentadiene with potassium amide in liquid ammonia was studied in order to determine the feasibility of this base system. Potassium amide was prepared from the ferric nitrate catalyzed reaction of potassium with liquid ammonia in a special apparatus described in the Chapter VI. Addition of 1, 4-pentadiene at -70° gave a yellow solution. Warming to -40° was attended by a reversible color change to deep red. After filtration of the solution into an nmr tube, nmr analysis at low temperature gave a very good spectrum of the pentadienyl anion. The spectrum was independent of temperature or color, and could be analyzed by first order methods to give the data recorded in Table VII.

Table VII. Nmr Data for the Pentadienyl Anion[a]



Proton	Chemical shift[b]	Mult.	Coupling constants
H_a	204	triplet	J_{ab} = 12 Hz
H_b	332	8 lines	J_{bc} = 9 Hz
H_c	98	doublet of doublets	J_{cd} = 3.5 Hz
H_d	123	doublet of doublets	J_{bd} = 16 Hz

[a] Recorded at -40° in liquid ammonia.

[b] Cps downfield from ammonia.

The coupling constants and the configuration agreed well with the results of Kloosterzeil (65a). The nmr observed by Bates for the same anion in THF reproduced the above spectrum at 15° but at 35° evidence for an exchange process which makes the terminal methylene protons equivalent is found in the observation of only a broad hump in the resonance region of these protons. At 40° the hump reduces to the doublet expected for equivalent methylene protons (59).

The same experiment was repeated for triene I. As has been the case with previous experiments, a very fast reaction destroyed the triene. The low temperature nmr showed no trace of triene

absorptions or of any new peaks even after being subjected to the computer average of transients (CAT) technique for 10 scans. Analysis of the residue after addition of ethanol revealed no dimers.

As in the alkyllithium experiments, it was thought worthwhile to try reactions with a hindered base, in this case lithium bis-trimethylsilylamide prepared from the reaction of n-butyllithium with the parent amine (66). The reaction with triene was performed in vacuo at room temperature. An nmr of the mixture after quenching with D_2O showed only a small amount of unreacted triene. Glc analysis failed to reveal the presence of dimers. A large amount of a musky smelling brown polymer was isolated.

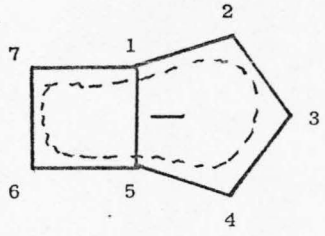
At this point any further attempts at producing the anion in moderately high concentration did not seem worthwhile. In order to ascertain whether or not the anion could be prepared from triene I at all, a high dilution experiment was set up. The experimental conditions were the same as those reported by Breslow in his pK_a experiments (9), except that the reaction was run in vacuo using an apparatus described in Chapter VI. A mixture of triene I and THF was slowly vacuum transferred into a very dilute ($<1\%$) solution of lithium dicyclohexylamide and tetramethylethylenediamine in THF at -78°. After addition was complete the mixture was quenched at -78° with methanol-O-d. Gas chromatography of the organic layer showed the presence of dimers III and IV and triene I in total yield of less than 5%.

The important thing to do was to determine whether either the dimers or the triene or both had incorporated deuterium. If they had it would be good proof that the anion was formed and was stable over the course of the addition since the only source of deuterium was present only at the quench. The analysis for deuterium incorporation was made by gas chromatography-mass spectroscopy. The cracking pattern for the dimers prepared as above showed a parent peak at m/e 182 corresponding to incorporation of two deuteria. The mass spectrum of the triene did show evidence of deuteration in the abnormally large peak at m/e 91 but isolation and ir analysis of the triene failed to exhibit any carbon-deuterium stretches in the expected positions. Also, this spectrum displayed absorptions other than those due to the triene implying an impurity inseparable under the preparative conditions used. A good explanation for the apparent discrepancies in the mass spectrum and infrared spectrum of the triene is not at hand as of this writing. The important result of this experiment is the characterization of the dideuterodimers, direct proof of the formation of free anion from triene I.

Discussion

Hückel Molecular Orbital theory and the advanced PPO-SCF-CI calculations discussed in Chapter Ia make definite predictions concerning the charge distribution in anion Ia. Both calculations predict greater than 70% of the charge to be almost evenly distributed at the 1, 3 and 5 positions. It was hoped that the experiments described

above would have enabled a test to be made of these predictions. An nmr of the anion would have given information about the charge densities at the 2, 3 and 6 positions as well as information concerning presence or absence of a ring current. Also, studies on the position of protonation of the anion would have given a chemical probe into the charge distribution of the this species. This assumes of course that formation of the products is kinetically controlled and that rates of protonation at the different carbons are determined by the charge density at those carbons. These conditions have been found to hold in other systems (67).



The many attempts at observing an nmr spectrum of the anion proved to be futile because of rapid polymerization of triene I. Interpretation of reactions of the anion with proton donors turned out not to be straightforward but these results and some thoughts on the polymerization reaction are given below.

Dimer Formation and the Site of Protonation of the Anion.

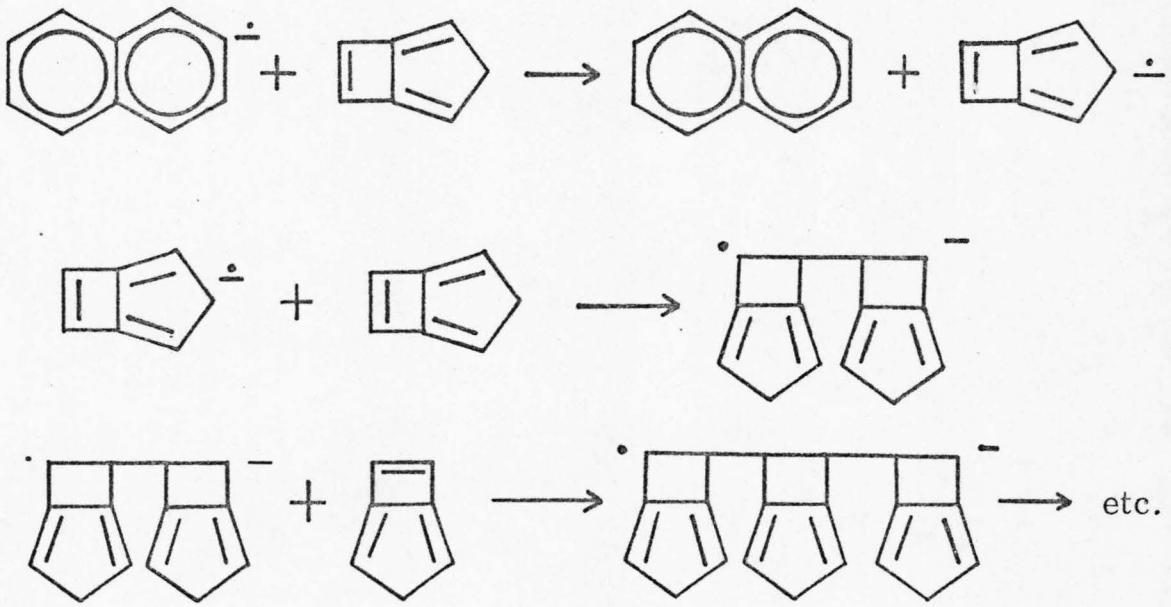
The formation of dimers III and IV in the reaction of triene with base strongly implies the intermediacy of triene II. This triene isomer can be formed from protonation of the anion at the 1 or 5 position.

The question arised as to whether reprotonation ever takes place at the 3 position to give back triene. This question may be answered in different ways depending upon the interpretation of the results.

The results of the reaction of I with potassium t-butoxide lead to the conclusion that reprotonation takes place solely at the 1 and 5 positions since no deuterium hydrogen exchange is observed at the 3 position under conditions where deuterium is incorporated into the dimers. The most likely explanation for this is that the charge density at the 1 and 5 positions is much higher than at the 3 position. Another rationale is that reprotonation is a very fast process and takes place within the solvent cage before the formed t-butanol has a chance to leave the vicinity of the 3 position. In other words, the preference in position of protonation is due to the unequal distribution of proton donating solvent molecules about the incipient anion, the distribution being higher about the 1 and 5 positions than at the 3 position because of the presence of the bulky t-butanol group. This explanation is valid only if the diffusion of the t-butanol away from the anion is slow compared to reprotonation. This interpretation is made credible by Cram's observation that a large difference in pK_a between solvent and substrate will favor reprotonation of the carbanionic system in the cage before it can pass into a symmetrical environment (68). In the present case the difference in pK_a between I and DMSO is on the order of 9 units. This is the same difference reported by Cram for the fluorenyl-DMSO system on which the above observation was based.

The high dilution experiment with dicyclohexylamide would have provided information on this problem since the anion was formed in a non-exchanging medium. However the results of this experiment are not reliable because of the contradictory spectral results. A distinction between the charge density and solvation explanations will have to be made upon the basis of further experiments.

Polymer Formation. Polymer is formed in high yield from the reaction of triene I with the naphthalene radical anion. A polymerization of the type elucidated by Scwarc may be operative here (69). The steps outlined below are typical for radical anion induced polymerizations.



This radical anion-incuded polymerization may also be implicated in the polymerization of I with t-butoxide, the alkyllithiums and the alkali metals. Precedents in each of the above cases have been listed (70).

Acidity of I. One of the goals of this research was to measure the acidity of I. However the lack of exchange at the methylene position and the failure to generate significant concentrations of Ia clearly precluded such a measurement.

CHAPTER IV

GAS PHASE ACIDITIES OF CONJUGATED HYDROCARBONS

Introduction

One of the aims of the present research was to determine the acidity of triene I relative to other conjugated systems. In this way it might be possible to test the validity of HMO predictions (Chapter Ia). However, attempts to generate anion Ia in solution met with only limited success because of the fast polymerization of triene I in basic media.

A logical alternative is to study acidities in the gas phase where there are no solvent effects and it is therefore possible to measure intrinsic acidities of molecules (8). In solution, acidities are measured in terms of pK_a units defined in Equation (1) where water is the standard base.

$$HA + H_2O \rightleftharpoons H_3O^{\oplus} + A^{\ominus}$$

$$pK_a = pH \quad \text{when} \quad \frac{[A^{\ominus}]}{[HA]} = 1 \tag{1}$$

Although for acids of pK_a greater than 14 water is not useful as a standard it is possible to extrapolate above 14 using other data (5). Inherent in all pK_a determinations is the problem of the effect of the solvent upon the energetics of the proton transfer. That pK_a's are dependent upon the solvent system has been amply demonstrated (71).

Ideally, measurement in the gas phase of the proton affinity of the conjugated base of the acid HA ($PA(A^-)$) as in Equation (2) gives a true measure of the intrinsic acidity of HA.

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

$$PA(A^-) = -\Delta H^0 \qquad (2)$$

Acidities measured in this manner are absolute in the sense that there is no arbitrary reference as in pK_a measurements. Proton affinities of anions may be determined directly from ΔG^0 for the reaction $AH + B^- \rightleftharpoons BH + A^-$ in which $PA(B^-)$ is known independently. $PA(A^-)$ may be calculated from the relationship $PA(B^-) - PA(A^-) = \Delta H^0$ where for proton transfer reactions $\Delta H^0 = \Delta G^0$ since ΔS^0 is probably zero (72).

The practical problems in studying gas phase reactions are substantial but can be overcome by rather sophisticated mass spectral techniques which unfortunately in the past were not available to organic chemists. However with the advent of ion cyclotron resonance spectroscopy (icr) (73), flowing afterglow techniques (74), and tandem mass spectrometry (75) the current literature abounds with descriptions of the reaction of organic ions in the gas phase (76). These techniques have been very useful in the determination of relative acidities and basicities. The potential precision of these determinations is reflected in the work of Aue in which relative basicities of amines were determined to ± 0.1 kcal/mole by icr spectroscopy (77).

Using icr techniques Brauman and Blair determined the relative acidities of alcohols (72), amines (78), and carbon acids (79). These workers found that aliphatic alcohols show an ordering of acidities which is the reverse of that in solution. The following is Brauman and Blair's order of relative acidities for alcohols and carbon acids: $(CH_3)_3COH > (CH_3)_2CHOH > C_2H_5OH > \phi CH_3 > CH_3OH > H_2O > \phi H$. In the gas phase, alcohol acidities are increased by increasing alkyl substitution while in solution the reverse is observed. The ordering in the gas phase may be correlated to stabilization of the charge on the oxygen by polarization of the alkyl groups. In solution the amount of energy gained by polarization is overshadowed by the large free energies of solution of the ions. The most striking aspect of the above ordering is that toluene is a better acid than water or methanol.

Recently, Bohme has determined the relative acidities of some carbon acids using the flowing afterglow technique (80). His results give the following order of acidities: $HC{\equiv}CH > CH_2{=}C{=}CH_2 > \phi CH_3 > H_2C{=}CHCH_3 > H_2O > \phi H > H_2 > NH_3$ and $\underline{n}\text{-}C_4H_9SH > CH_3NO_2 > C_5H_6 > CHCl_3 > CH_3COCH_3 > CH_3CN > CH_3SOCH_3 > CH_2Cl_2 > HC{\equiv}CH \cong \underline{t}\text{-}C_4H_9OH > C_2H_5OH > CH_3OH > CH_2{=}C{=}CH_2$.

It appears from the results of these workers that conjugate bases of carbon acids may be formed from proton transfer reactions of the conjugate acids with strong bases. Accordingly, an investigation of the relative gas phase acidities of triene I, 1,4-pentadiene, cycloheptatriene, cyclopentadiene, and toluene was initiated in

collaboration with Professor J. L. Beauchamp, utilizing icr spectroscopy. An additional objective was proton to determine proton affinities for the anions of these compounds.

Description of Ion Cyclotron Resonance Spectroscopy Techniques. The details of the instrumentation and experimental techniques of icr spectroscopy have been described thoroughly elsewhere (81). The generation and observation of ions takes place in the cyclotron resonance cell (Figure 10). The entire cell is contained in an evacuated chamber and located in the field of an electromagnet. Ions generated from suitable precursors by electron bombardment in the source region of the cell are drifted by crossed magnetic and electric fields into the analyzer region where they are detected by power absorption from a radio frequency electric field applied perpendicular to the magnetic field. The frequency is dependent upon the mass and charge of the ion and the strength of the magnetic field. By varying the magnetic field while holding a constant radio frequency, it is possible to obtain a mass spectrum.

During the time the ions spend in the icr cell (~2 ms) there is opportunity for collision or reaction with the neutral precursor or any other species present. The extent of reaction depends both on the ion transit time and the partial pressure of the neutral reactant. It is possible to follow the course of ion molecule reactions simply by recording the mass spectrum at different pressures. Disappearance of one ion while another appears implies that the two are chemically coupled. Energetics of the reaction may be determined from

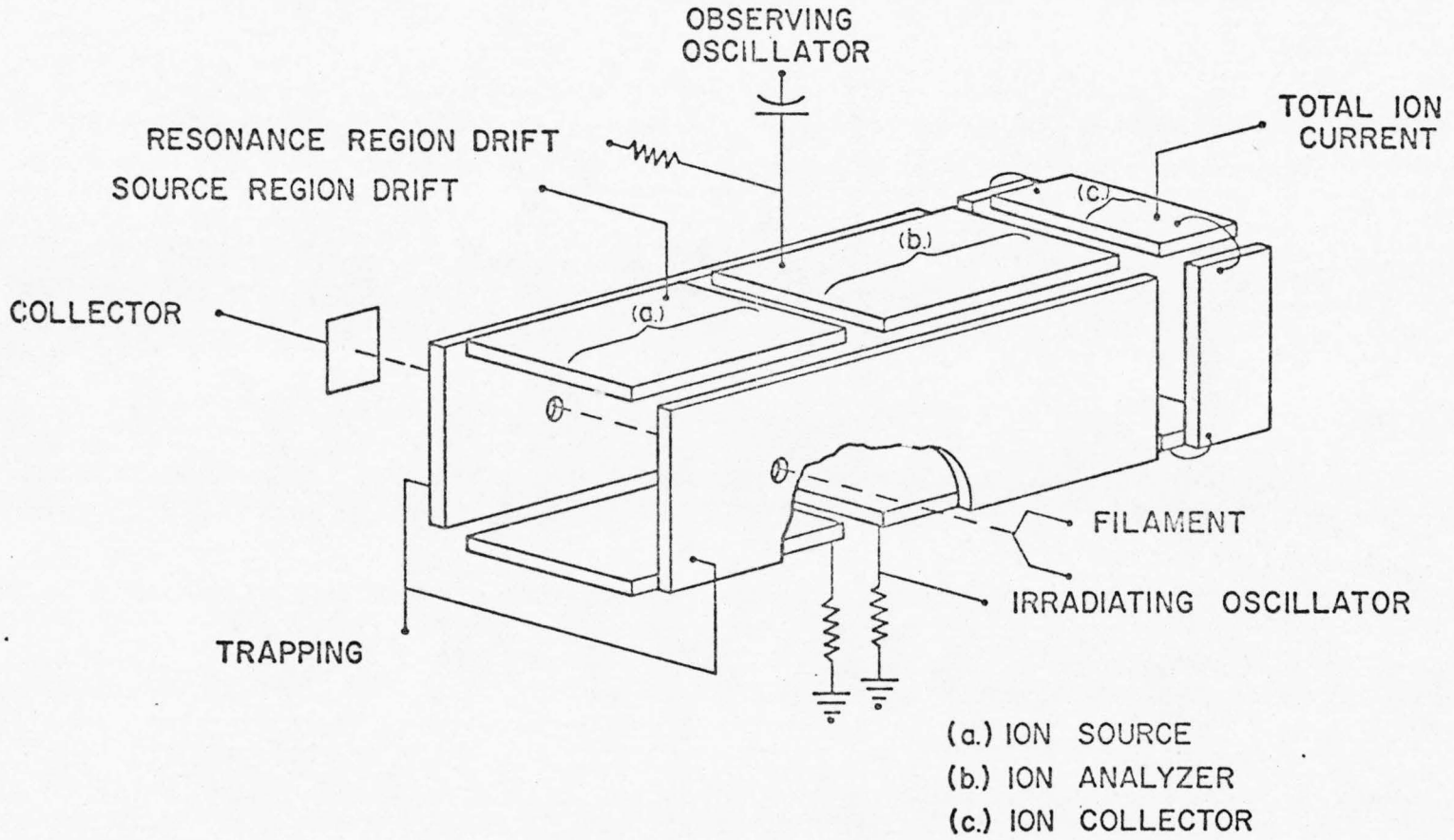


Figure 10. Cutaway view of cyclotron resonance cell

equilibrium measurements or from the rates for the forward and reverse reactions.

A powerful complementary technique for determining reaction pathways is ion cyclotron double resonance. Double resonance experiments involve the observation of one ion species while irradiating a second at its cyclotron resonant frequency with an auxiliary radio frequency oscillator. This irradiation increases the kinetic energy of the second ion. If the second ion is coupled chemically to the observed ion by a reaction, such as $A^- + B \rightleftharpoons C^- + D$ then addition of energy perturbs the system, resulting in a change of intensity of the observed ion. The direction of the change in intensity of the observed ion may be related to the energetics of the reaction. These relations, the underlying rationale for which has been described elsewhere (82) may be summarized as follows: (1) a decrease in intensity is associated with an exothermic or thermoneutral reaction; (2) an increase in intensity is associated with either an endothermic or exothermic reaction; and (3) an endothermic reaction must give a positive change at low irradiating field strength. Double resonance techniques are sufficiently sensitive to observe a 1% change in reaction rate and the results may be checked for consistency by observation of each ion in turn while irradiating the others.

It is necessary to qualify these considerations in the case of high irradiating field strengths. Removal of the reactant ion from the cell under such conditions will lead to a negative response regardless of whether or not the reaction is endothermic or

exothermic, provided the process is occurring under the conditions of the experiment.

Both pressure dependence and double resonance techniques were employed to determine relative acidities in the work described below.

Results

In the present study it was hoped that relative proton affinities of the conjugated hydrocarbon anions might be determined from the ΔG^0's of the proton transfer reactions of the neutrals with the anions. In order to insure the accuracy of the results, it was important that methods for the generation of the anions be on hand which took into account the relative inefficiency of negative ion formation in the gas phase. There are two general methods commonly employed: (1) direct formation of the anion from the neutral by electron impact and (2) reaction of the neutral with a strong base.

The direct method is preferred because the only reactants would be the hydrocarbons themselves. There are three processes by which anions may be generated by electron impact:

1) Resonance capture

$$AH + e^- \longrightarrow AH^-$$

2) Dissociative electron capture

$$AH + e^- \longrightarrow A^- + H\cdot$$

3) Ion pair production

$$AH + e^- \longrightarrow A^- + H^+ + e^- \cdot$$

Ion formation from 1 and 2 is a resonant process, i.e., the electrons must be of a well-defined energy characteristic of the particular neutral involved but typically in the range 0-10 v electron energy. Process c has no such energy restriction and occurs over the range 10-100 v electron energy.

Unfortunately, of the conjugated hydrocarbons only cyclopentadiene was observed to give the corresponding anion upon electron impact. This process, most likely a dissociative capture reaction, commenced at 1.8 v and peaked at 2.5 v electron energy (uncalibrated, see Figure 11).

For the other hydrocarbons method 2 had to be employed. The experiments of Brauman and Blair (72, 79) and Bohme (80) suggested that hydrocarbon anions might be formed by proton transfer reactions of the neutrals with the strong base methoxide (CH_3O^-). Accordingly the reaction of CH_3O^- with the conjugated hydrocarbons was investigated.

Generation of Primary Bases. Methoxide may be generated easily in the gas phase from methyl nitrite by dissociative electron capture (81). At 10^{-5} torr a sufficient number of scattered electrons are trapped in the icr cell to lead to production of CH_3O^- in abundance. At higher pressures (Figure 12) ion molecule reactions between CH_3O^- and methyl nitrite cause a decrease in CH_3O^- and a

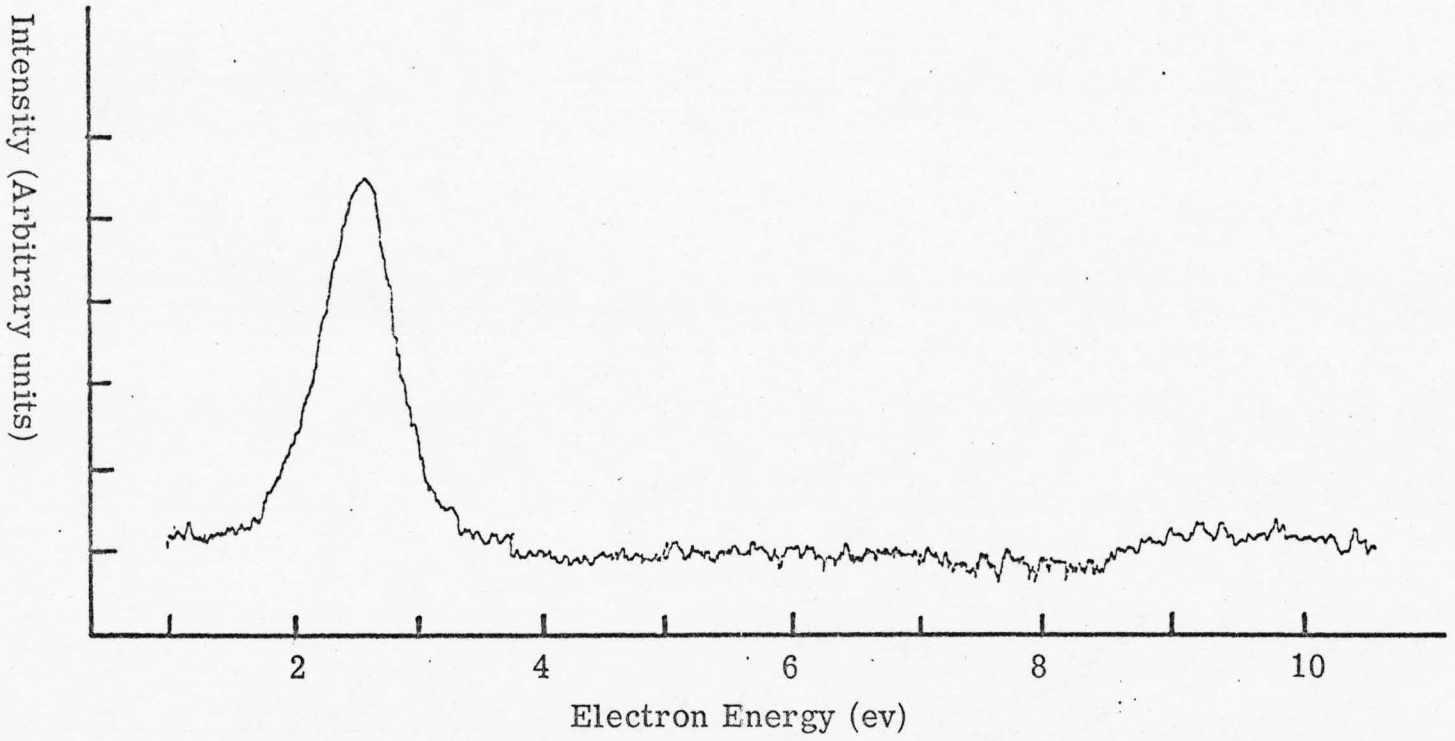


Figure 11. Ion intensity of $C_5H_5^-$ vs. electron energy

corresponding increase in m/e 46 and 60 ions. The first corresponds to NO_2^- while the second may be either CH_2ONO^- or $CH_2NO_2^-$. Although the structure cannot be definitely assigned, the later is more likely because of its expected stability. It is not likely that $CH_2NO_2^-$ arises from CH_3NO_2 impurity because of the method of preparation and purification of methyl nitrite (see Chapter VI). The sequence of reactions initiated by dissociative electron capture are summarized below:

$$CH_3ONO + e^- \longrightarrow CH_3O^- + NO\cdot$$

$$CH_3O^- + CH_3ONO \longrightarrow CH_3OCH_3 + NO_2^-$$

$$CH_3O^- + CH_3ONO \longrightarrow CH_2ONO^- \text{ or } CH_2NO_2^- + CH_3OH$$

In order to minimize reaction of CH_3O^- with methyl nitrite, the initial pressure of methyl nitrite was maintained below 10^{-5} torr.

In the course of experimentation it became necessary to utilize bases other than CH_3O^-. Table VIII lists these bases along with their sources and conditions for generation.

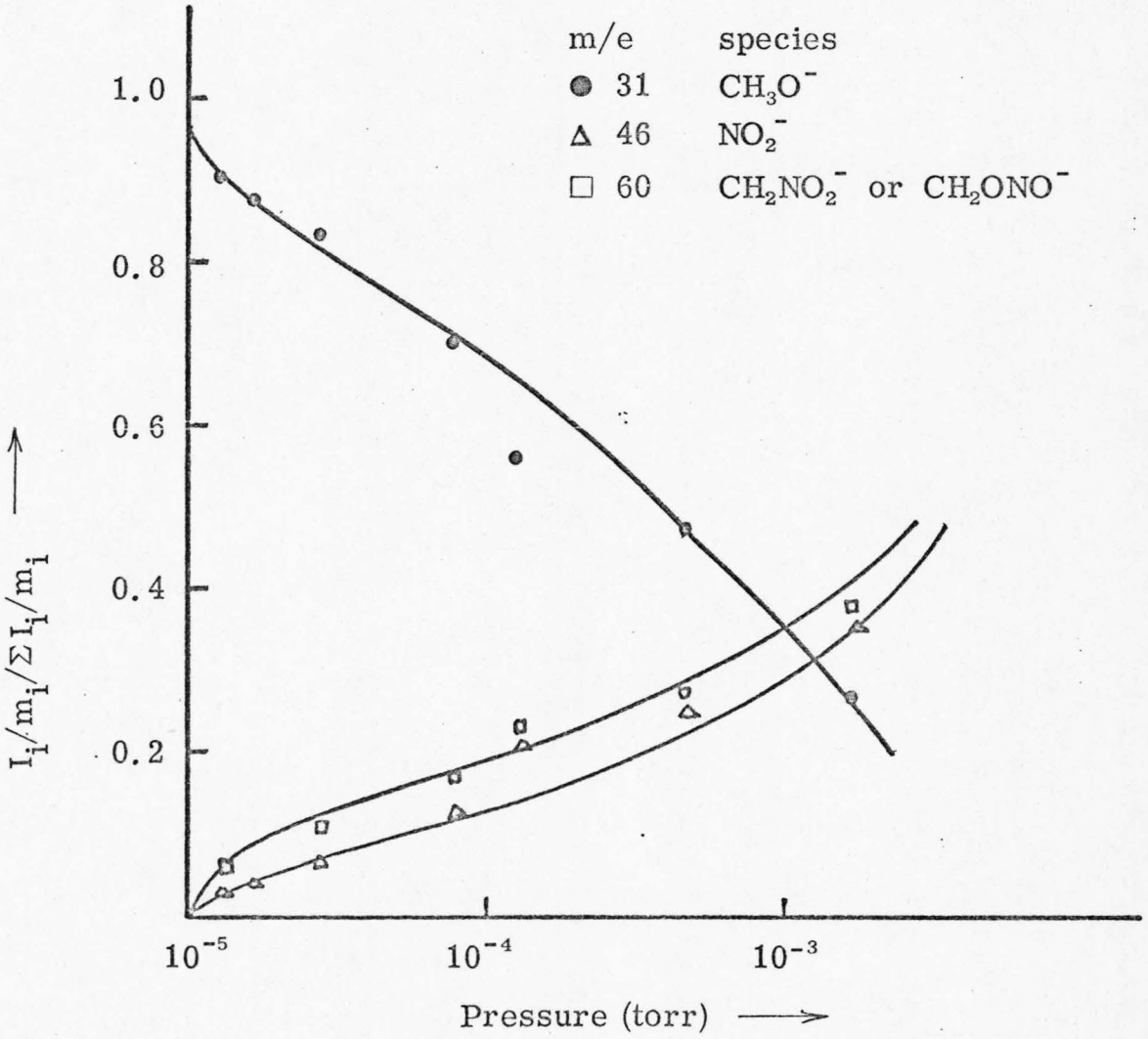


Figure 12. Variation of ion abundances with pressure for CH_3ONO at 70 ev

Table VIII. Gas Phase Negative Ion Sources

Ion	Source	Electron energy	Reference
CH_3O^-	CH_3ONO	10-70 ev	This work, 81
$C_2H_5O^-$	C_2H_5ONO [a]	10-70 ev	83
OH^- [b]	H_2O	6.5 ev	84
PH_2^-	PH_3	7.3 ev	85
AsH_2^-	AsH_3	7.1 ev	86
$C_5H_5^-$	C_5H_6	2.5 ev	this work
SiH_3^-	SiH_4	9.5 ev	87

[a] Contained ethanol.

[b] Generated by reaction of H^- with H_2O.

Generation of Hydrocarbon Anions. All hydrocarbons reacted rapidly ($k = 10^{-10} - 10^{-9}$ cm^3 molecule^{-1} sec^{-1}) with methoxide to produce the corresponding anions. This is indicated for a mixture of methyl nitrite and triene I by the variation of ion abundance with pressure given in Figure 13. Although isotopically labelled reactants were not examined, it was assumed that only the aliphatic hydrogens were abstracted. This is reasonable because Bohme (80) and Brauman (79) have shown that vinylic hydrogens are much less acidic than the methyl hydrogens in toluene.

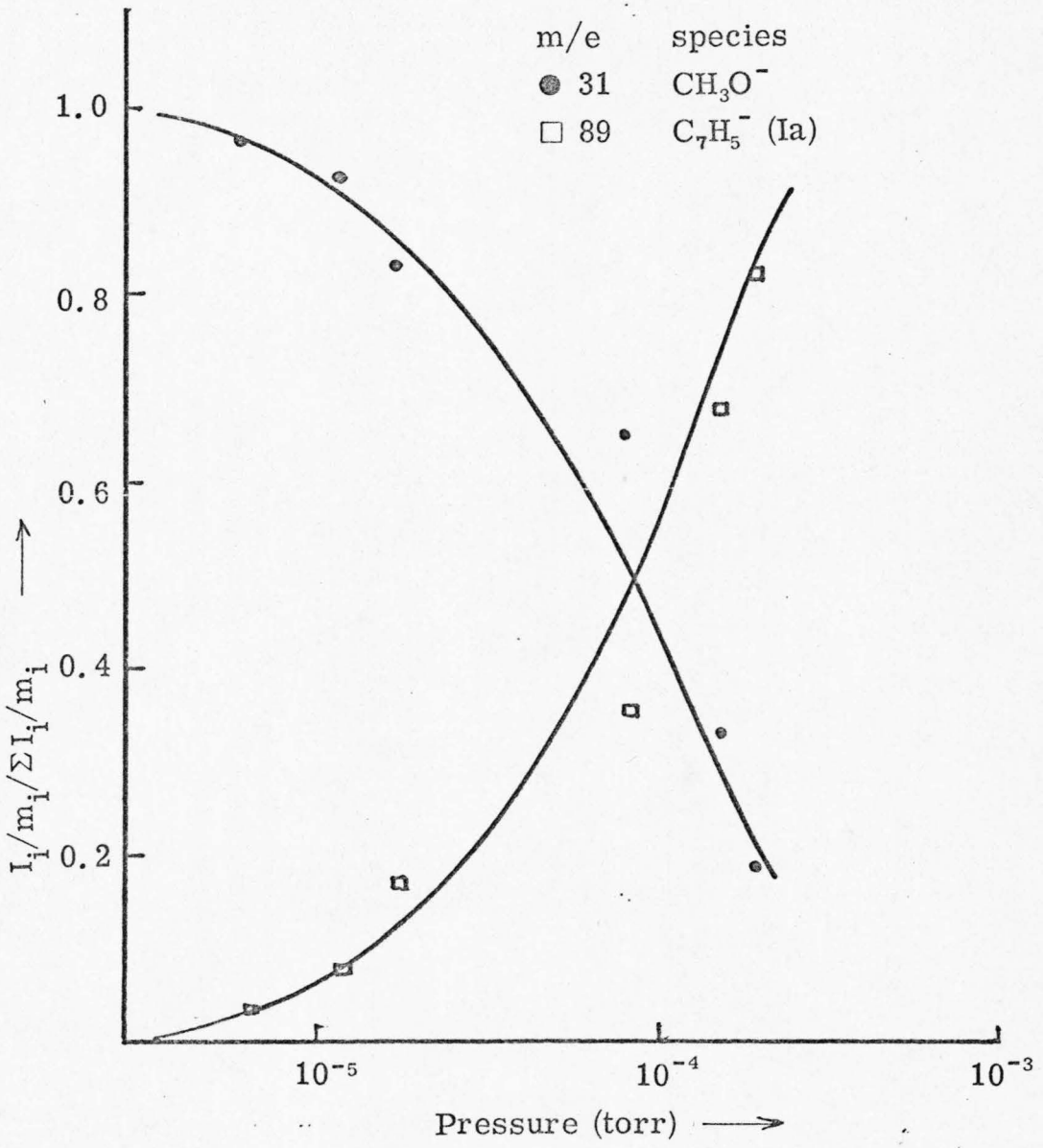
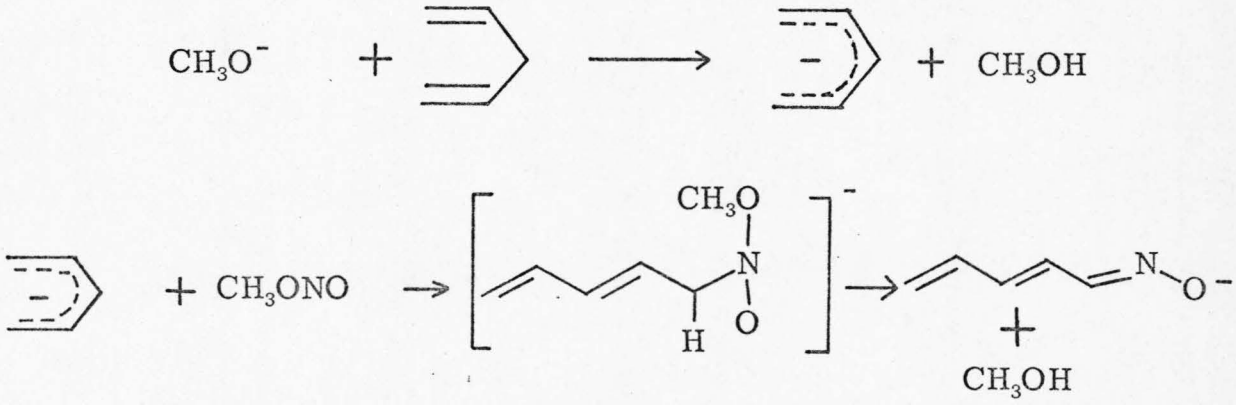


Figure 13. Variation of ion abundances with pressure for a 1:1 mixture of I and CH_3ONO

The conjugate bases of cyclopentadiene and triene I generated by the reaction of the corresponding neutral with CH_3O^-, were not observed to react further with methyl nitrite. In mixtures of 1, 4-pentadiene, cycloheptatriene and toluene, respectively, with methyl nitrite, however, products 29 mass units heavier than the hydrocarbon anion were observed. For example, reactions of the mixture of 1, 4-pentadiene with methyl nitrite are given below:

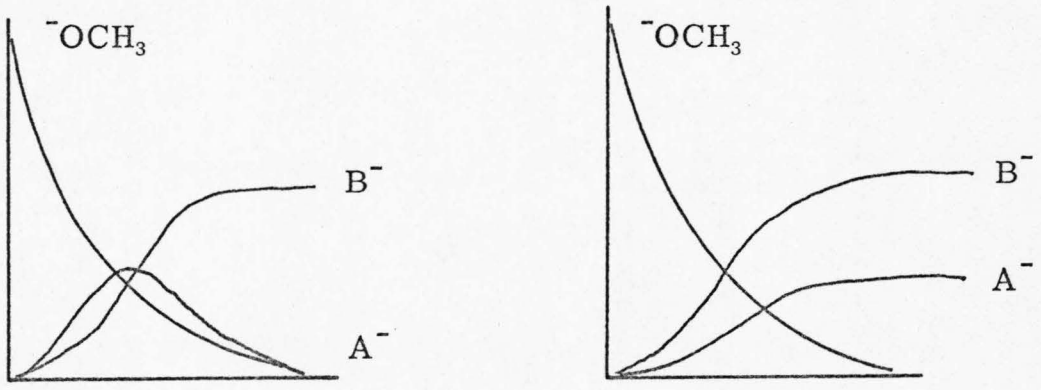


Double resonance experiments confirmed the occurrence of these reactions.

The discrimination displayed in the above addition-elimination reaction is interesting. A possible explanation for the fact that this reaction is not observed for triene I and cyclopentadiene may be that reaction is only accessible to those anions containing negative charge at a primary carbon. On steric grounds this explanation is reasonable since addition reactions are favored for primary systems.

Admittedly this does not account for the reactivity of the cycloheptatrienyl system but at this point rearrangement of the cycloheptatrienyl anion to the benzylic anion before reaction cannot be ruled out. The results of the reaction of 3, 3-dideutero-1, 4-pentadiene with methyl nitrite would divulge the position of addition for the pentadienyl system. Addition from the primary position should result in a monodeuterated product while addition from the three position should give undeuterated product.

Relative Acidities and Proton Affinity Determination. In the present investigation mixtures of anions and their neutrals were generated by the reaction of CH_3O^- or OH^- with binary mixtures of hydrocarbons. Ideally, after reaction with the base is complete the dependence of the ion abundances on total pressure will be determined by the magnitude of the difference in proton affinities of the formed anions. For the reaction $A^- + BH \rightleftharpoons AH + B^-$ where the neutrals are in 1:1 molar ratio, when $PA(A^-) - PA(B^-)$ is greater than 4 kcal/mole the dependence of the ion abundance as a function of pressure will be as in case A below; case B (equilibrium situation) holds when $PA(A^-) - PA(B^-)$ is less than or equal to 4 kcal/mole. From case A may be inferred the relative acidities of AH and BH while for case B relative proton affinities for A^- and B^- may be determined from the equilibrium constant for the reaction given by $A_{(B^-)}/A_{(A^-)}$.



A B

Analysis of the results of the actual experiments upon binary mixtures of conjugated hydrocarbons was not straightforward. Unfortunately, proton transfer reactions between the hydrocarbon anions and their neutrals were found to be exceedingly slow. For instance, referring to Figure 14 which gives the ion abundance as a function of pressure for the reaction of CH_3O^- with a 1:1 molar mixture of triene I and 1, 4-pentadiene, it is seen that although the intensity of CH_3O^- decreases rapidly due to reaction with the hydrocarbons, the abundances of the formed hydrocarbon anions change only slowly with pressure. This is inferred to be due to the slowness of proton transfer between the hydrocarbon anions and the neutrals. Neither an equilibrium condition nor a clear cut dominance of one anion is attained in this reaction. However from the slow increase in the abundance of the m/e 67 (pentadienide) ion relative to the m/e 89 (Ia) ion the acidity ordering 1, 4-pentadiene > I is inferred.

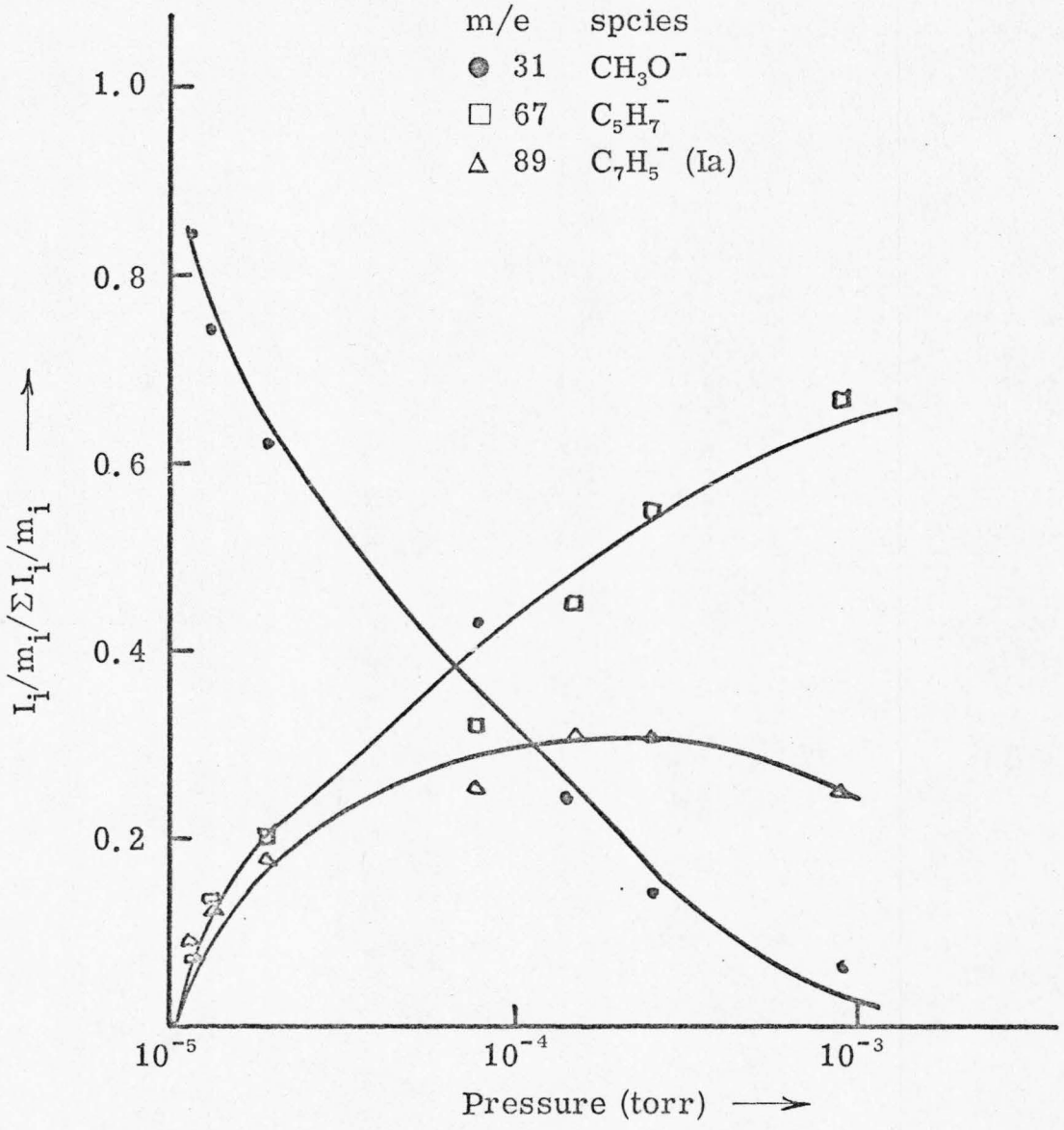
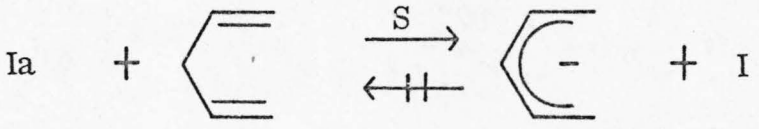


Figure 14. Variation of ion abundances with pressure for a 1:1:1 mixture of CH_3ONO, I, and 1, 4-pentadiene

(The addition elimination product from pentadienide and methyl nitrite accounted for $<5\%$ of the ion intensity under the conditions of the above reaction.) This ordering is confirmed by double resonance experiments. An increase in ion intensity was observed for the m/e 89 peak when m/e 67 was irradiated; a decrease in intensity of the m/e 67 peak was observed while irradiating m/e 89. The slowness of the proton transfer reactions was apparent from the weak double resonance signals observed. From the pressure dependence and double resonance experiments the reaction path is inferred to be the following:



From experiments similar to the above the following order of acidities can be derived: cyclopentadiene > 1, 4-pentadiene > triene I. Toluene and cycloheptatriene were observed not to participate in proton transfer reactions with the other hydrocarbons studied and consequently could not be placed in the derived order of acidities.

In order to provide a quantitative measure of hydrocarbon acidities the above studies were extended to include reference species whose acidities are reasonably well established. The results of these experiments are summarized in Table IX. From these results the following order of relative acidities was derived:

Table IX. Gas Phase Reactions

Mixture	Primary base	Reaction [b]	Method used to infer reaction [c]
C_5H_6, MN [a]	CH_3O^-	$CH_3O^- + C_5H_6 \xrightarrow{f} C_5H_5^- + CH_3OH$	P
C_5H_8, MN	CH_3O^-	$CH_3O^- + C_5H_8 \xrightarrow{f} C_5H_7^- + CH_3OH$	P
C_7H_6, MN	CH_3O^-	$CH_3O^- + C_7H_6 \xrightarrow{f} C_7H_5^- + CH_3OH$	P
C_7H_8, MN	CH_3O^-	$CH_3O^- + C_7H_8 \xrightarrow{f} C_7H_7^- + CH_3OH$	P
C_7D_8, MN	CH_3O^-	$CH_3O^- + C_7D_8 \xrightarrow{f} C_7D_7 + CH_3OH$	P
MN, C_5H_6, C_5H_8	CH_3O^-	$C_5H_6 + C_5H_7^- \overset{s}{\rightleftharpoons} C_5H_5^- + C_5H_8$	P, DR
MN, C_5H_8, C_7H_6	CH_3O^-	$C_5H_8 + C_7H_5^- \overset{s}{\rightleftharpoons} C_5H_7^- + C_7H_6$	P, DR
MN, C_2H_5OH, C_5H_8	CH_3O^-	$C_2H_5O^- + C_5H_8 \overset{f}{\rightleftharpoons} C_5H_7^- + C_2H_5OH$	P, DR
MN, C_2H_5OH, C_7H_6	CH_3O^-	$C_2H_5O^- + C_7H_6 \overset{f}{\rightleftharpoons} C_7H_5^- + C_2H_5OH$	P, DR
MN, C_2H_5OH, C_7H_8	CH_3O^-	$C_2H_5O^- + C_7H_8 \overset{f}{\rightleftharpoons} C_7H_7^- + C_2H_5OH$	P, DR
MN, H_2S, C_5H_6	CH_3O^-	$H_2S + C_5H_5^- \overset{f}{\rightleftharpoons} HS^- + C_5H_6$	P, DR
MN, CH_3NO_2, C_5H_6	CH_3O^-	$C_5H_6 + CH_2NO_2^- \xrightarrow{s} C_5H_5^- + CH_3NO_2$	P
MN, CH_3NO_2, C_7H_6	CH_3O^-	$CH_3NO_1 + C_7H_5^- \xrightarrow{s} CH_2NO_2^- + C_7H_6$	P
H_2O, C_7H_8, C_5H_8	OH^-	$C_7H_8 + C_5H_7^- \rightleftharpoons C_5H_8 + C_7H_7^-$	P, DR
MN, C_5H_6, CH_3CHO	CH_3O^-	$C_5H_6 + CH_2CHO^- \xrightarrow{f} C_5H_5^- + CH_3CHO$	P

C_5H_8, CH_3CHO	CH_2CHO^-	$C_5H_8 + CH_2CHO^- \rightsquigarrow C_5H_7^- + CH_3CHO$	P
C_2H_5ONO, SiH_4, C_5H_8	$C_2H_5O^-$	$SiH_3^- + C_5H_8 \rightleftharpoons SiH_4 + C_5H_7^-$	P, DR
SiH_4, CH_3CHO	SiH_3^-	$SiH_3^- + CH_3CHO \rightleftharpoons SiH_4 + CH_2CHO^-$	DR
H_2O, SiH_4, C_5H_8	OH^-	$SiH_3^- + C_5H_8 \rightleftharpoons SiH_4 + C_5H_7^-$	P, DR
C_2H_5ONO, SiH_4, C_5H_6	$C_2H_5O^-$	$SiH_3^- + C_5H_6 \rightleftharpoons SiH_4 + C_5H_5^-$	P
AsH_3, C_5H_6	AsH_2^-	$AsH_2^- + C_5H_6 \xrightarrow{f} AsH_3 + C_5H_5^-$	P
H_2O, C_7H_8, C_7D_8	OH^-	$C_7H_7^- + C_7D_8 \rightleftharpoons C_7H_7D + C_7D_7^-$	P, DR
MN, C_7H_8, C_7D_8	CH_3O^-	$C_7H_7^- + C_7D_8 \rightleftharpoons C_7H_7D + C_7D_7^-$	P, DR
MN, CH_3CHO, CH_3NO_2	CH_3O^-	$CH_2CHO^- + CH_3NO_2 \xrightarrow{s} CH_2NO_2^- + CH_3CHO$	P, DR
MN	CH_3O^-	$CH_3O^- + MN \xrightarrow{f} CH_3OCH_3 + NO_2^- + CH_2NO_2^-$	P
MN, C_5H_8	CH_3O^-	$C_5H_7^- + MN \xrightarrow{f} C_5H_6NO^- + CH_3OH$	P, DR
MN, C_7H_8	CH_3O^-	$C_7H_7^- + MN \xrightarrow{f} C_7H_6NO^- + CH_3OH$	P, DR
MN, C_7D_8	CH_3O^-	$C_7D_7^- + MN \xrightarrow{f} C_7D_6NO^- + CH_3OH$	DR

[a] MN ≡ CH_3ONO.

[b] Where C_5H_6 ≡ cyclopentadiene; C_5H_8 ≡ 1, 4-pentadiene; C_7H_6 ≡ triene I; C_7H_8 ≡ cycloheptatriene; C_7D_8 ≡ toluene-d_8; f ≡ fast reaction; s ≡ slow reaction.

[c] Where P ≡ pressure dependence; DR ≡ double resonance.

$H_2S > C_5H_6 > CH_3NO_2 > 1,4\text{-}C_5H_8 > I > C_2H_5OH > CH_3OH > H_2O$;

cyclo-$C_7H_8 > C_2H_5OH$; $\phi CH_3 > CH_3OH$.

From the data in Table X and the established relative order, the following limits can be placed on the proton affinities of several of the anions of interest:

$$350 \text{ kcal/mole} < PA(C_5H_5^-) < 360 \text{ kcal/mole}$$

$$362 \text{ kcal/mole} < PA(C_5H_7^-, \text{ Ia, cyclo-}C_7H_7^-) < 377 \text{ kcal/mole}$$

$$PA(\phi CH_2^-) < 385 \text{ kcal/mole}$$

In the case of cyclopentadienide ($C_5H_5^-$) a more precise proton affinity may be calculated independently from the appearance potential for its formation by dissociative electron capture. The thermodynamic cycle given below gives a value of 354 kcal/mole for $PA(C_5H_5^-)$:

$$\begin{array}{rcl} e^- + C_5H_6 & \longrightarrow & C_5H_5^- + H\cdot \quad AP(C_5H_5^-) \\ H\cdot & \longrightarrow & H^+ + e^- \quad IP(H\cdot) \\ \hline C_5H_6 & \longrightarrow & C_5H_5^- + H^+ \quad PA(C_5H_5^-) \end{array}$$

$$\begin{aligned} PA(C_5H_5^-) &= AP(C_5H_5^-) + IP(H\cdot) \\ &= 41 + 313 \\ PA(C_5H_5^-) &= 354 \text{ kcal/mole} \end{aligned}$$

This value is in very good agreement with the estimated proton affinity from the proton transfer reactions.

Table X. Thermodynamic Quantities of Some Simple Acids

Species	Bond strength	EA (radical)	PA (anion)
H_2O	119[a]	42[b]	390[o]
CH_3OH	102[a]	30[c]	385[o]
C_2H_5OH	102[a]	39[d]	377[o]
HF	136[e]	80[f]	369
SiH_4	80[g]	28[o]	365
PH_3	80[i]	29[j]	364[o]
CH_3NO_2			361[h]
AsH_3	76[l]	29[m]	360[h]
H_2S	90[a]	53[n]	350[o]

[a] J. A. Kerr, Chem. Rev., 66, 465 (1966).

[b] L. M. Branscomb, Phys. Rev., 148, 11 (1966).

[c] P. Kriemler, S. E. Buttrill, Jr., J. Amer. Chem. Soc., 92, 1123 (1970).

[d] J. M. Williams, W. H. Hamill, J. Chem. Phys., 49, 4467 (1968).

[e] Reference 94.

[f] R. S. Berry, C. W. Reimann, J. Chem. Phys., 38, 1540 (1963).

[g] B. deB. Darwent, "Bond Dissociation Energies in Simple Molecules", NSRDS-NBS, National Bureau of Standards, Washington, D. C. (1970).

[h] From the ordering given by Eyler.[1] ($PA(AsH_2^-)$ = $PA(CH_2NO_2^-)$ - 0.3 = $PA(PH_2^-)$ - 3.4 = $PA(SiH_3^-)$ - 4.2) and $PA(PH_2^-)$ = 364 from Table X.

[i] Computed from appearance potential at 2.2 ev for $PH_3 \rightarrow PH_2^- + H\cdot$ by M. Halmann, I. Platzner, J. Phys. Chem., 73, 4376 (1969) and $EA(PH_2\cdot)$.

[j] Reference 93.

[l] John R. Eyler, Personal communication from J. L. Beauchamp.

[m] K. C. Smythe, determination from photodetachment, personal communication from John I. Brauman.

[n] B. Steiner, J. Chem. Phys., 49, 5097 (1968).

[o] Determined from the other two quantities (see text).

Electron affinities of radicals may be calculated from knowledge of proton affinities using the following thermodynamic formulation:

$$\begin{array}{ccccc} R\text{–}H & \xrightarrow{PA} & R^- & + & H^+ \\ \Big\downarrow D(RH) & & & & \Big\uparrow -EA(R\cdot) \\ R\cdot + H\cdot & & \xrightarrow{IP(H\cdot)} & & R\cdot + H^+ + e^- \end{array}$$

$$EA(R\cdot) = IP(H\cdot) + D(RH) - PA(R^-)$$

For cyclopentadiene where the methylenic carbon-hydrogen bond strength may be estimated to be 78 ± 3 kcal/mole (89) and $PA(C_5H_5^-)$ is 354 kcal/mole the electron affinity of the radical calculates to be 37 ± 3 kcal/mole.

Discussion

Hydrocarbon Acidities. Where valid comparisons can be made, the relative gas phase acidities of the hydrocarbons parallel their solution acidities. Thus, cyclopentadiene is a much better acid than either 1, 4-pentadiene or triene I. Unfortunately, cycloheptatriene cannot be compared here because no proton transfer reactions could be observed for its anion with other hydrocarbons. The difference in proton affinity between cyclopentadienide and Ia is on the order of ten to twenty kcal/mole. The difference in acidity between cyclopentadiene and triene II is ten pK_a units (9) which correspond to 14 kcal/mole. Assuming triene II and triene I to have comparable acidities, the solution and gas phase energetics for proton loss are quantitatively similar. This result suggests that solvation does not greatly affect relative acidity for small conjugated hydrocarbons. Ritchie has shown that for large, conjugated hydrocarbons such as fluoradene, definite solvent effects are observed in acidity studies (88).

The acidities reported here are consistent with HMO predictions of anion stabilities (Chapter I). Cyclopentadiene, for example, is much more acidic than its acyclic analog 1, 4-pentadiene, an indication of the special stability derived from the cyclic 6π electron system. Also, the enhanced acidity of cyclopentadiene relative to triene I is consistent with the prediction of the modified Hess method of only a small amount of aromatic character for anion Ia (see

Chapter Ib). However, Brauman has pointed out that associating the acidity of an acid with the stability of its conjugate base can be misleading (72). In other words, the high acidity of cyclopentadiene is not necessarily due to the stability of the anion. It could possibly be due to a low bond dissociation energy of the methylenic carbon-hydrogen bond. However such effects are not operative in these cases (Table XI). The bond strength of all the hydrocarbons are within 10 kcal/mole of each other.

Proton Transfer Reactions. Failure to observe facile proton transfer reactions between hydrocarbon acids and bases is not well understood. Similar observations have been reported by other investigators (79, 80). Ritchie has postulated that slow proton transfer in solution may be explained by least motion considerations (90). The least motion principle holds that, other things being equal, activation energies for reactions which require substantial geometric and bonding changes in the transition state will be higher than for those that do not (91). The effect will be observable unless factors such as hydrogen bonding or solvation compensate for the rise in energy.

These arguments cannot be directly applied to gas phase proton transfer reactions, since such processes nominally do not possess an activation energy and in fact have rate constants which decrease with increasing translational energy of the reactant ion. It is however not unreasonable to imagine that proton transfer reactions will be unfavorable if they are accompanied by major

Table XI. Bond Strengths and Electron Affinities for Some Conjugated Hydrocarbon Species

Hydrocarbon	Methylenic C–H bond strength (kcal/mole)	Electron affinity of the radical		Other est.
		upper limit	lower limit	
Cyclopentadiene	78[a]	41	31	37 ± 3[f]
1,4-Pentadiene	75[b]	22	12	–
Triene I	75[c]	22	12	–
Cycloheptatriene	73[d]	24	14	–
Toluene	85[e]		13	22

[a] Reference 89.

[b] Estimated assuming 20 kcal/mole stabilization energy from two allylic systems.

[c] Estimated from a and d.

[d] G. Vincow, H. J. Dauben, Jr., F. R. Hunter, W. V. Volland, J. Amer. Chem. Soc., 91, 2823 (1969) and A. G. Harrison, L. R. Howness, H. J. Dauben, Jr., F. P. Lossing, J. Amer. Chem. Soc., 82, 5593 (1960).

[e] J. A. Kerr, Chem. Rev., 66, 465 (1966).

[f] This thesis.

[g] A. F. Gaines and F. M. Page, Trans. Faraday Soc., 59, 1266 (1963).

structural reorganization. This is particularly true if the intermediates involved in the gas phase proton transfer reactions are relatively short lived. It is noteworthy that similar effects have been observed in proton transfer reactions involving neutral n-donor bases. For example, the reaction

where M is a neutral n-donor base (e. g., acetone) is not observed to occur rapidly, even when significantly exothermic (92).

The limited quantitative data available do not permit general conclusions to be drawn which allow one to predict whether exothermic proton transfer reactions involving simple acids and their conjugate bases (e. g., H_2O, H_2S, CH_3OH) in which little structural reorganization occurs tend to be rapid (10^{-10} - 10^{-9} cm^3 $molecule^{-1}$ sec^{-1}). Proton transfer reactions between these species and conjugated hydrocarbons tend to be fast with the possible exception of nearly thermoneutral reactions. Proton transfer reactions between conjugated hydrocarbons, however, occur slowly if at all.

Future Work. Proton transfer reactions between conjugated carbon acids and bases appear to be intolerably slow for accurate determinations of proton affinities from equilibrium measurements. An alternative procedure would be to measure proton affinities directly from the appearance potentials for the formation of the anions

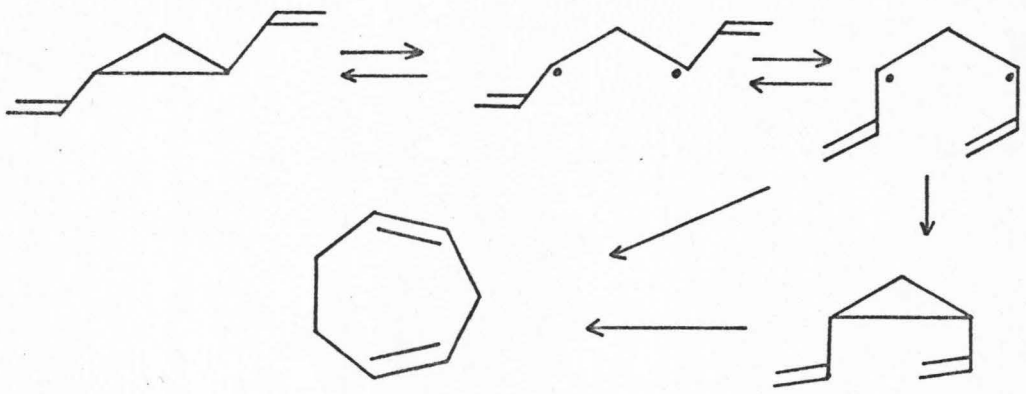
by dissociative electron capture. This procedure worked well for cyclopentadienide but data for the other hydrocarbon systems is lacking. Some careful work in this area would prove quite rewarding.

Another alternative is to determine the quantities in the thermodynamic cycle for proton affinity mentioned above. Electron affinities of radicals may be determined from photodetachment studies (93) while bond energies can be determined by classical methods (94) or from appearance potentials (95).

CHAPTER V

Part 1. Kinetics of the cis and trans-1, 2-Diethynylcyclopropane Rearrangements to Bicyclo[3. 2. 0]hepta-1, 4, 6-triene

During the flow pyrolysis experiments described in Chapter II it was noted that cis-XVIII rearranged at a much lower temperature than trans-XVIII. This behavior is qualitatively similar to the rearrangements of cis and trans divinyl cyclopropanes (96) and cyclobutanes (97) to cycloheptadienes and cyclooctadienes, respectively. The cis-isomers undergo valence isomerization much more quickly than the trans-isomers. Indeed in the cyclopropyl case the cis-isomer cannot be isolated whereas the trans rearrangement can be studied conveniently at 200°. The accepted explanation for this behavior is that the cis-isomer is undergoing a fast, Cope rearrangement which is accelerated by favorable geometry of the cis linkage. The trans-isomer has to undergo cleavage of the 1, 2 bond and then rotation to a cis conformation in order to achieve the same favorable geometry. In this case whether reaction takes place from the cis-diradical or from the cis-isomer itself is not known. The higher temperatures required for rearrangement of the trans-isomer reflect the relatively large energy requirement for cleavage of the 1, 2-carbon-carbon bond to give the diradical.



As discussed in Chapter Ia the concerted rearrangement of cis-XVIII to triene I is predicted by Woodward-Hoffmann rules to be energetically unfavorable. However the large temperature differences for the rearrangements implies that the cis-XVIII rearrangement is much more favorable than that for trans-XVIII. Since comparison of rates and activation parameters in the above divinyl cases gave information concerning the mechanisms of the reactions, it was decided to study the kinetics of the diacetylene transformations so that inferences could be made about the mechanisms.

Results

The gas phase kinetics of the cis- and trans-XVIII valence isomerizations were conducted in a conventional static system described in Chapter VI.

For trans-XVIII the reaction was studied in the temperature range 200°-240°. Runs were carried out at a total pressure of

70 mm on a mixture of trans-XVIII, the internal standard cycloheptane, and pentane diluent. The results of four runs in a well conditioned unpacked pyrex reactor are given in Table XII and a typical first order rate plot is reproduced in Figure 15. Rates were evaluated by the method of least squares and the correlation factor for the fit of the data to the integrated first order rate expression was greater than 0.99 in all cases.

In order to test the homogeneity of the reaction, runs 2 and 4 were carried out in a pyrex vessel packed with sections of pyrex tubing so that the surface to volume ratio was increased by a factor of ten over the unpacked reactor. The six rates from the packed and unpacked vessels, fitted to the integrated Arrhenius equation, gave a good straight line, implying that surface effects for the trans-XVIII to triene I transformation are negligible. The Arrhenius activation parameters were determined by the method of least squares. They are: E_a = 43.0 kcal/mole; log A = 15.53; $\Delta S^{\ddagger}$ (220°) = 9.6 eu. A run at 214.5° in a quartz vessel was within 3% of the rate for that temperature in the pyrex unpacked reactor. This is further proof of the homogeneity of the reaction. In all cases triene I was the sole product but no rates for the appearance of I were determined because I slowly polymerized under the reaction conditions.

The cis-XVIII kinetics were studied in much the same way as the trans-XVIII kinetics except that the temperature range was much lower (96°-136°) and toluene was used as internal standard. The rates for four runs and a typical first order plot are given in Table

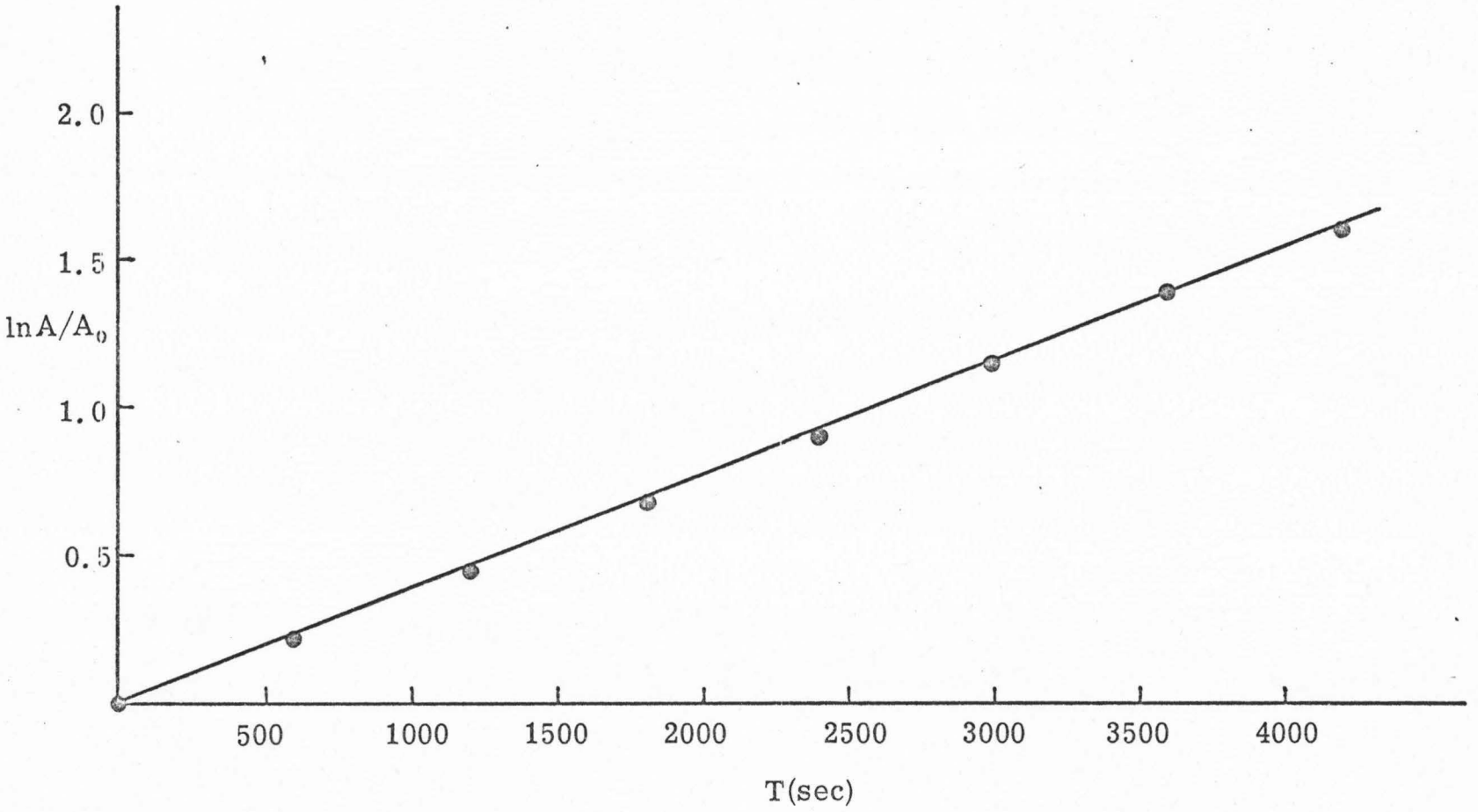


Figure 15. First Order Rate Plot for Disappearance of trans-1, 2-diethynylcyclopropane at 229.8°

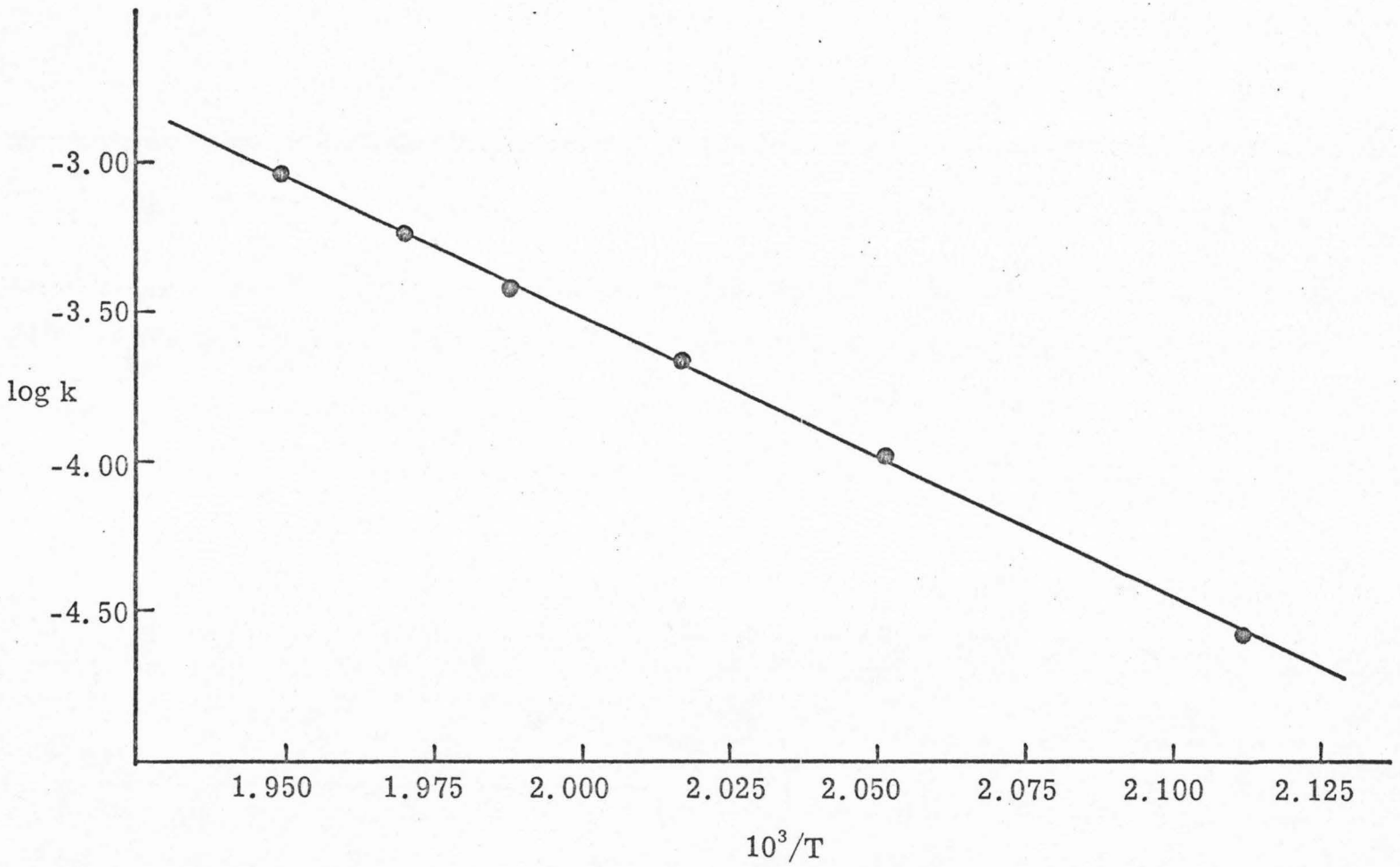


Figure 16. Arrhenius Plot for the Disappearance of trans-1,2-diethynylcyclopropane

Table XII. Rate Constants for the Isomerization of trans-1, 2-Diethynylcyclopropane (XVIII) to Bicyclo[3.2.0]-hepta-1, 4, 6-triene (I)

Run	Temperature °C	10^4 k (sec^{-1})	ρ [a]
1 [b]	239.8	9.23	0.999
2 [c]	234.6	5.73	0.999
3 [b]	229.8	3.84	0.999
4 [c]	222.6	2.19	0.999
5 [b]	214.5	1.06	0.999
6 [d]	214.5	1.09	0.996
7 [b]	200.3	0.259	0.991

[a] Correlation factor.

[b] Unpacked pyrex reactor.

[c] Packed pyrex reactor.

[d] Unpacked quartz reactor.

Table XIII. Rate Constants for the Isomerization of cis-1, 2-Diethynylcyclopropane (XVIII) to Bicyclo[3.2.0]-hepta-1, 4, 6-triene (I)

Run	Temperature °C	10^4 k (sec^{-1})	ρ [a]
1	136.1	11.4	0.999
2	136.1	11.9	0.999
3	126.1	5.43	0.999
4	111.1	1.80	0.998
5	96.1	0.556	0.999
6 [b]	119.0	6.03	0.998

[a] Correlation factor.

[b] Packed pyrex reactor; runs 1-5 in unpacked pyrex reactor.

XIII and Figure 17, respectively. At these low reaction temperatures it was possible in one case to determine the rate of appearance of I and it was found to be very close to the rate of disappearance of cis-XVIII at the same temperature. The Arrhenius plot gave a good straight line (Figure 18) and the Arrhenius parameters calculated by the method of least squares are E_a = 22.7 kcal/mole; log A = 9.23; and $\Delta S^{\ddagger}$ = -18.9 eu (119°). However determination of the rate in the packed vessel showed the cis-XVIII reaction to be surface dependent. The measured rate at 119° (6.03×10^{-4} sec^{-1}) was 1.35 times faster than the predicted rate (4.47×10^{-4} sec^{-1}) from the Arrhenius

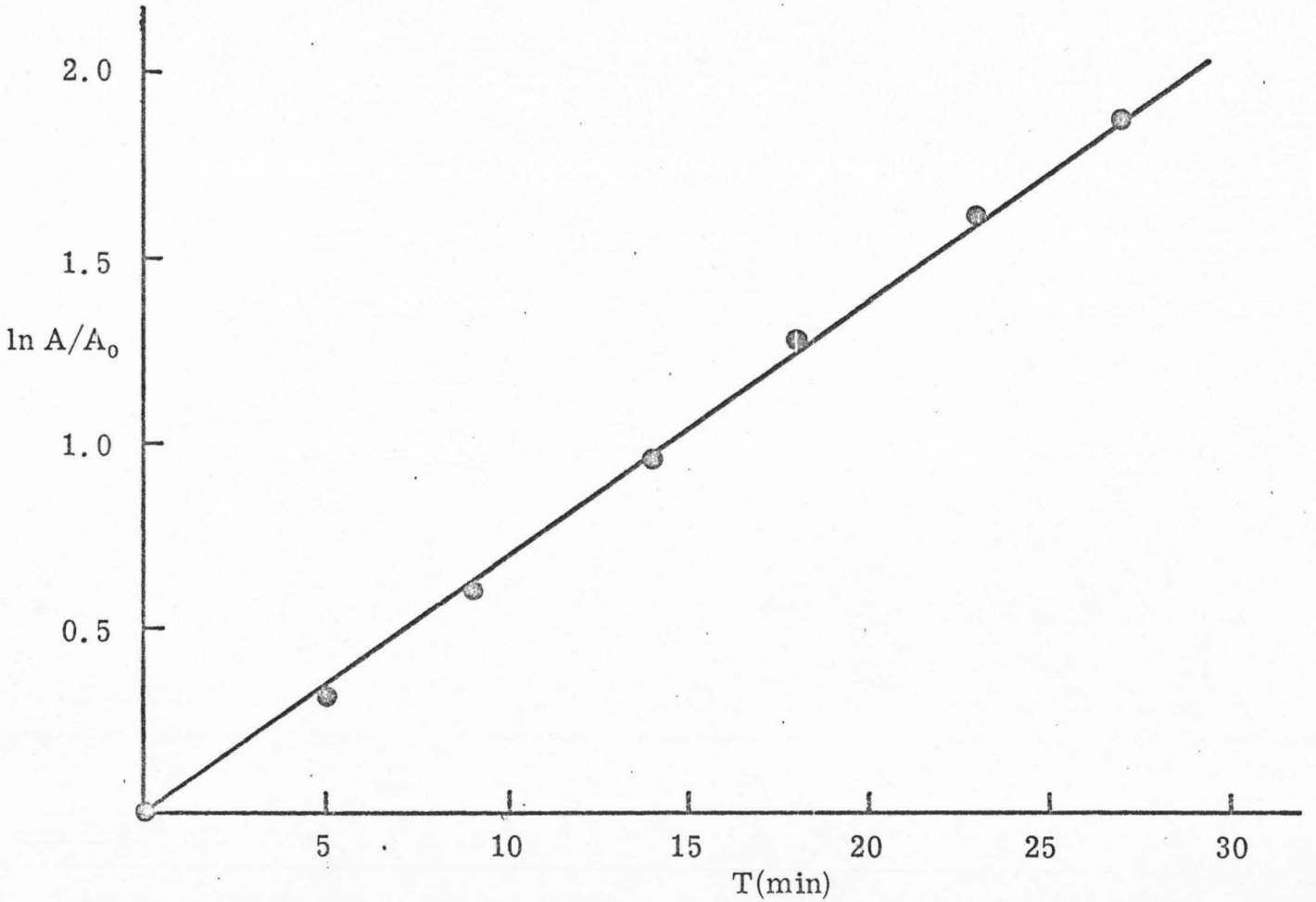


Figure 17. First Order Rate Plot for the Disappearance of cis-1, 2-Diethynylcyclopropane at 136.1°

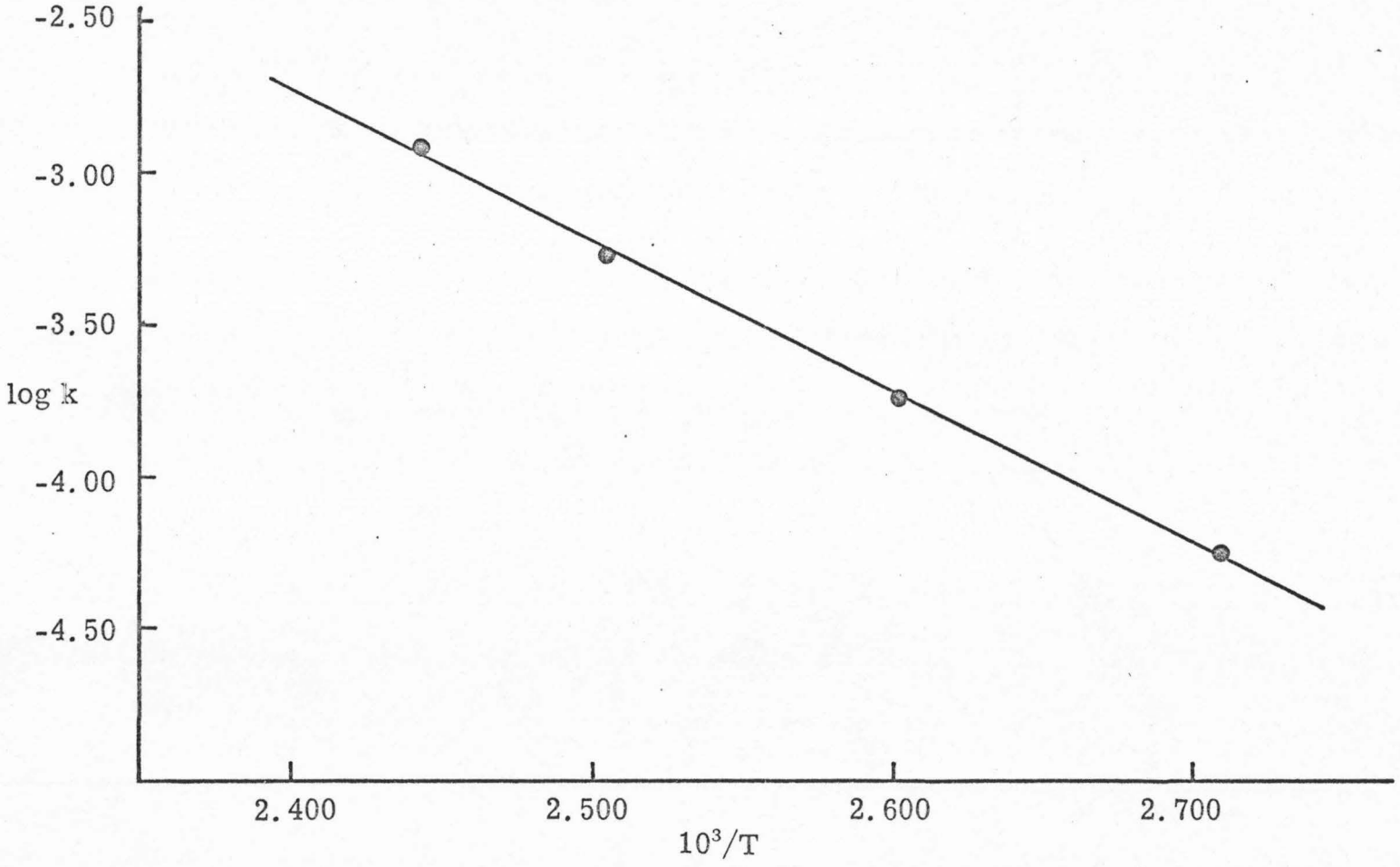


Figure 18. Arrhenius Plot for Disappearance of cis-1, 2-Diethynylcyclopropane

equation. This in itself is not an unreasonable surface factor but in the same run it was noted that although cis-XVIII disappeared in a first order fashion, less than 10% of the expected amount of triene was formed. That triene was relatively stable under the packed reactor conditions was shown in the trans-XVIII pyrolyses. This implies that two different mechanisms are taking place in the cis-XVIII reaction (see Discussion).

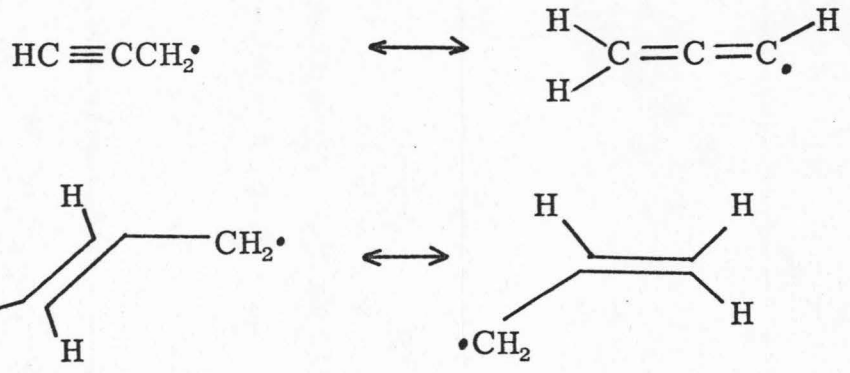
Discussion

Trans-XVIII. The activation energy and entropy of activation of the trans-XVIII reaction are consistent with formation of the diradical as rate determining step. For comparison purposes the activation parameters for some cyclopropyl and cyclobutyl systems are listed below.

	E_a (kcal/mole)	$\Delta S^{\ddagger}$ (eu)	Ref
trans-methylethyl-cyclopropane	60.1	+6.8	98
trans-divinyl-cyclopropane	32.1	-6.2	96a
trans-divinyl-cyclobutane	34.0	-1.7	97a
cis-divinylcyclobutane	23.1	-11.7	97b

The energies of activation for the trans-divinyl systems are 25-27 kcal/mole lower than that for the dialkyl system. If this difference in energy corresponds to a stabilization of the transition

state leading to the diradical by twice the allylic resonance energy, the stabilization energy due to one allylic resonance is then 12.5-13.5 kcal/mole. This value is in good agreement with a different determination of this quantity (99). Application of the same rationale to the trans-XVIII system leads to a value of 8 kcal/mole for the propargyl resonance energy. The difference in resonance energies between the allylic and propargyl systems is 5 kcal/mole which agrees very well with the 4.0 kcal/mole reported by Martin (100) from the pyrolyses of β,γ olefinic and acetylenic peresters. The lower stabilization energy of the propargyl system is probably due to the fact that the two contributing canonical forms of the radical, one acetylenic and the other allenic, are of unequal energies whereas in the allylic system the forms are of equal energy. In the usual resonance interpretation, the more contributing forms of equal energy, the more stable the hybrid structure (101).



The value for the entropy of activation is also consistent with initial diradical formation, since positive entropies in cyclopropane ring pyrolyses are usually associated with bond cleavage to this species. Comparison with the trans-divinyl systems however leads one to an apparent anomaly: the values here are quite a bit lower than that for trans-XVIII. This apparent inconsistency is easily explained. The low value for the divinyl cases is due to serious restriction of rotation about the radical centers in the transition state in order to maintain overlap between the developing radical orbitals and the p lobes of the vinyl systems. In the case of the acetylene group no such restrictions are necessary because the centrosymmetric nature of the carbon-carbon triple bond guarantees that overlap will take place in any rotational state. Therefore one would expect the ethynyl substituted systems to display entropies of activation similar to alkyl substituted systems and indeed the value for trans-methylethylcyclopropane is close to that for trans-XVIII. These results are also quite consistent with those of Martin (101). He found entropies of activation to be negative in cases where allylic radicals were being formed and positive (6 eu) where propargyl radicals were being formed.

Cis-XVIII Kinetics. The activation parameters obtained for the cis-XVIII reaction are not consistent with either a concerted or diradical mechanism. The latter is ruled out by the relatively low magnitude of the energy of activation (23.0 kcal/mole). The value expected for diradical formation in the case of cis-XVIII should be

only a few kilocalories lower than that for trans-XVIII (43.0 kcal/mole) because of the difference in ground state energies due to the cis linkage. Also, no trans-XVIII was observed in the pyrolysis of cis-XVIII. One would expect in the case of diradical formation at least some rotation and closure to give trans-XVIII which would be stable under the reaction conditions.

While the energy of activation for the cis-XVIII reaction is reasonable for a concerted process the entropy of activation is not. Usually observation of a negative entropy of activation for a reaction suggests a rigid transition complex in which some free rotations are lost relative to the ground state (102). For instance, in the case of the 1,5-hexadiyne to dimethylenecyclobutene rearrangement (20) rotation about the 3,4 bond has to be restricted so that the acetylenic groups might attain the cisoid conformation necessary for further reaction. The entropy of activation for this reaction is -9 eu. However in the case of cis-XVIII, the acetylenic groups are locked in the orientation necessary for interaction. Since no rotations are lost in the presumed cyclic transition state, one would not expect the entropy of activation to be any more negative than the 1,5-hexadiyne case. The value obtained (-18 eu) then is quite unreasonable for any unimolecular process.

It appears that the most reasonable explanation for these results is that the reaction is surface catalyzed. This is suggested by the very low values for both the activation energy and the entropy of activation and by the surface dependence of the rates and products.

By definition the activation energy for a catalyzed reaction is expected to be smaller than that for similar uncatalyzed systems. For instance, the activation energy for the 1, 5-hexadiyne system is 34.4 kcal/mole whereas for cis-XVIII, it is only 23.0 kcal/mole. The low A factor is quite consistent with the need for restrictions on the orientation of the molecule as it approaches the active site on the surface. Probably catalysis obtains only for preferred orientations (103). There are other examples of surface dependent reactions which display low activation energies and unreasonably low A factors (Table XIV). For instance, the cis, trans-isomerization of 2-butene was found by Anderson et al. (104) to have an activation energy of 52.0 kcal/mole and log A equal to 11.0. The surface independent parameters obtained by Rabinovitch and Michel (105) are E_a = 62.8 kcal/mole and log A = 13.78. One very striking aspect of the figures given in Table XIV is the way that the rate constants for each isomerization remain very close while the Arrhenius parameters are very different. This implies that the $\Delta G^{\ddagger}$'s for these reactions are quite close regardless of the surface effects.

The rate and product dependence on the surface may be discussed most easily in terms of the kinetic scheme given below.

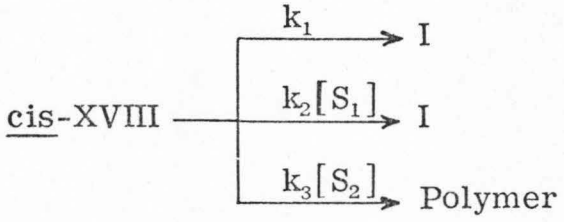
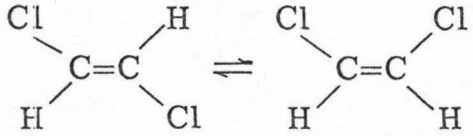
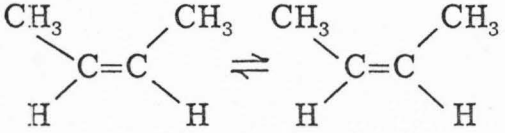


Table XIV. Activation Parameters for Some Surface Catalyzed Gas Phase Reactions

Reaction	log A	E_a (kcal/mole)	T°C	log k	Ref.
	2.32	16.0	826	-1.90	106
"	12.68[a]	55.3	826	-2.12	107
	0.3	18	700	-5.32	108
"	11.0	52.0	700	-5.23	104
"	13.78[a]	62.8	700	-5.82	105

[a] Preferred values.

For unpacked reactor

$$\frac{d[\underline{cis}\text{-XVIII}]}{dt} = k_1[\underline{cis}\text{-XVIII}] + k_2[S_1][\underline{cis}\text{-XVIII}]$$

$$= (k_1 + k_2[S_1])[\underline{cis}\text{-XVIII}]$$

For packed reactor

$$\frac{d[\underline{cis}\text{-XVIII}]}{dt} = (k_1 + k_2[S_1] + k_3[S_3])[\underline{cis}\text{-XVIII}]$$

In this scheme $[S_1]$ is the surface component of the reaction for the unpacked reactor and $[S_2]$ is that for the packed reactor. These surfaces are different in that reaction on the unpacked surface gives I whereas reaction on the packed surface gives only polymer. This behavior may be due to incomplete conditioning of the packed reactor. Mr. T. H. Morton (109) experienced great difficulty in conditioning the packed reactor for the 3, 3-dimethylcyclopropene system. Since the surface component is constant for each reactor, the composite rates are still first order overall.

In the packed reactor, since polymer appears to account for >90% of the products, $k_3[S_2]$ must be greater than k_1 or $k_2[S_1]$. The reverse holds for the unpacked system but it is not possible to decide whether k_1 or $k_2[S_1]$ is more important. The possibility here is that the observed rate is actually a composite of the surface rate (k_2) and of the gas phase rate (k_1). It was thought initially that composite rates would not give a good fit to the Arrhenius equation because of the complexity of the overall equation for parallel processes: $k_1 + k_2 = A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT)$. However,

upon combining the rates for an idealized concerted process (E_a = 30.0 kcal/mole, log A = 13.0) with those probable for a surface process (E_a = 16.0 kcal/mole, log A = 5.0) it was possible to obtain an Arrhenius plot which displayed a good straight line (ρ = 0.999, Figure 19) and parameters (E_a = 23.6 kcal/mole; log A = 9.08) close to those observed for cis-XVIII. This exercise shows how it might be possible for cis-XVIII to display a good Arrhenius plot yet still be kinetically complex. Thus it is not possible here to ascribe the behavior of cis-XVIII completely to a surface effect. However the unreasonably low value for the A factor is good indication that the surface component for this system is quite important. This conclusion obviates any conclusions which might be drawn concerning the mechanism of the cis-XVIII transformation.

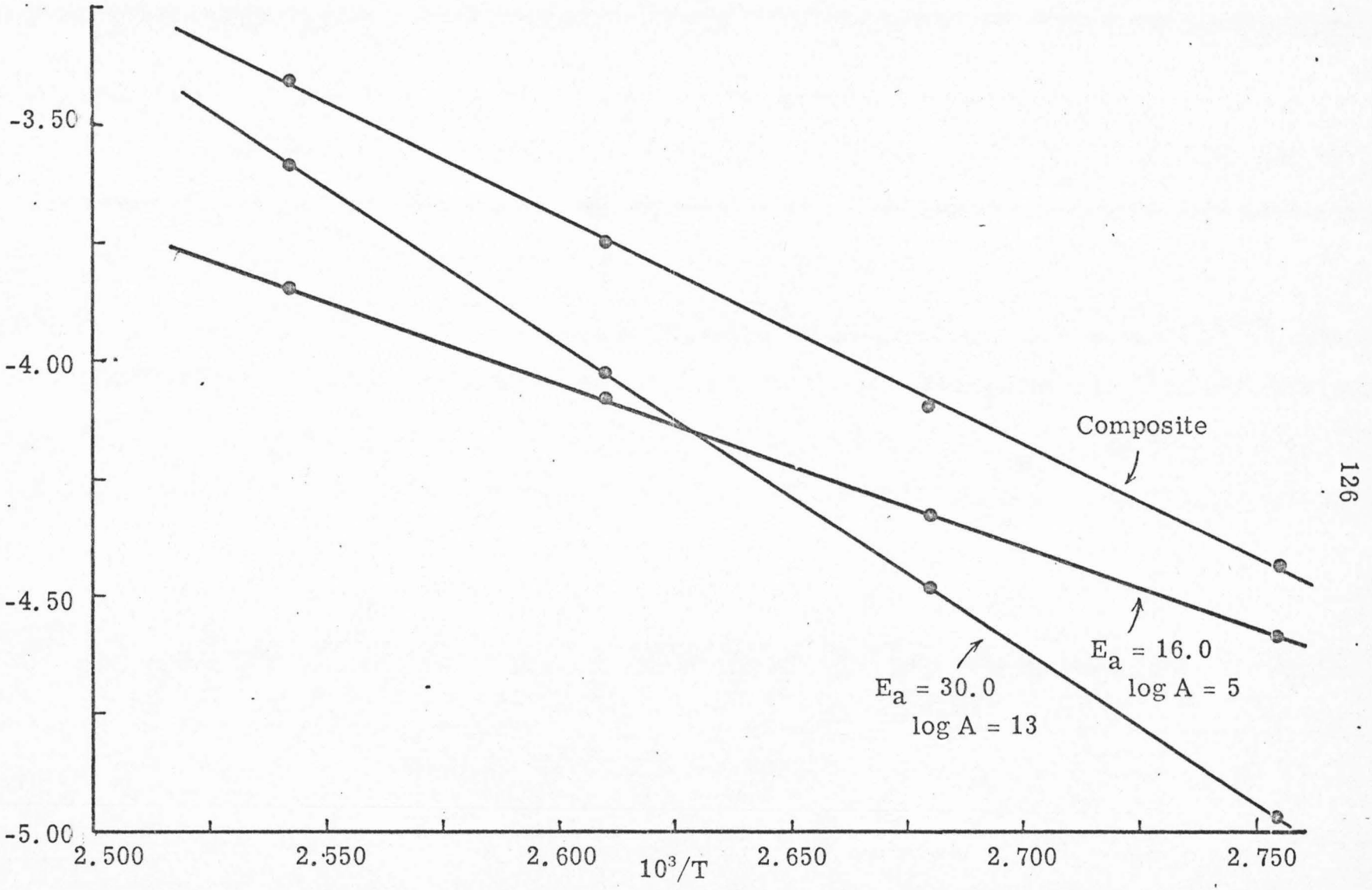
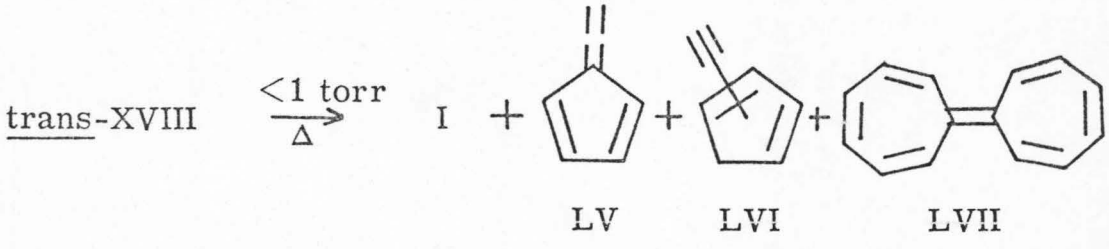


Figure 19. Derived Arrhenius Plot for Parallel Concerted and Surface Reactions

CHAPTER V

Part II. Pressure Dependent Formation of Bicyclo[3.2.0]hepta-1,4,6-triene, Fulvenallene, and Ethynylcyclopentadiene in the Pyrolysis of trans-1,2-Diethynylcyclopropane

Under preparative conditions, fulvenallene LV, ethynylcyclopentadiene LVI and heptafulvalene LVII are produced in addition to triene I in the vacuum flow pyrolysis of trans-XVIII. Early experimentation showed a marked dependence of the product distribution on effective system pressure. Lower pressure favored the formation of LV and LVI at the expense of the triene. These crude results suggested the intermediacy of a vibrationally activated species, most likely chemically activated triene I for which further reaction to LV and LVI was competitive with collisional deactivation. In order to gain more definite proof of the intermediacy of such a species an examination of the pressure and temperature dependence of the formation of reaction products was undertaken. The results described below confirmed the intermediacy of chemically activated triene in both the low pressure vacuum flow and static systems.



A species is chemically activated if the energy necessary for its reaction to other products is derived from its exothermicity of formation. For instance, in the reaction A → B →C, the minimum amount of energy B will contain immediately after its formation will be equal to the sum of the activation energy E_1 and the difference in the heats of formation of A and B, E_2 (Figure 20).

There are two things that energized B can do: (1) it can collide with other molecules and lose part or all of its excess energy (collisional deactivation) or (2) it can react to give C if the excess energy is greater than the activation energy E_3. The relative importance of each path will depend upon the number of collisions suffered by B^* and the intrinsic rate of reaction of B* to C. On the macro scale the collisional frequency is directly related to the pressure of the reaction system. Therefore lower relative pressure should favor further reaction of B* to C while higher pressure will favor deactivation of B* to ground state B.

According to RRKM theory the intrinsic rate of the B* to C reaction is dependent upon the amount of excess energy in B* and the number of vibrational modes in B (110). Quantitatively this relation is given by Equation (1):

$$k = A\left(\frac{E - E_0 + E_Z^+}{E + E_Z}\right)^{s-1} \qquad (1)$$

where A is the high pressure frequency factor for the B → C transformation, E_0 is the energy of activation for the B to C reaction,

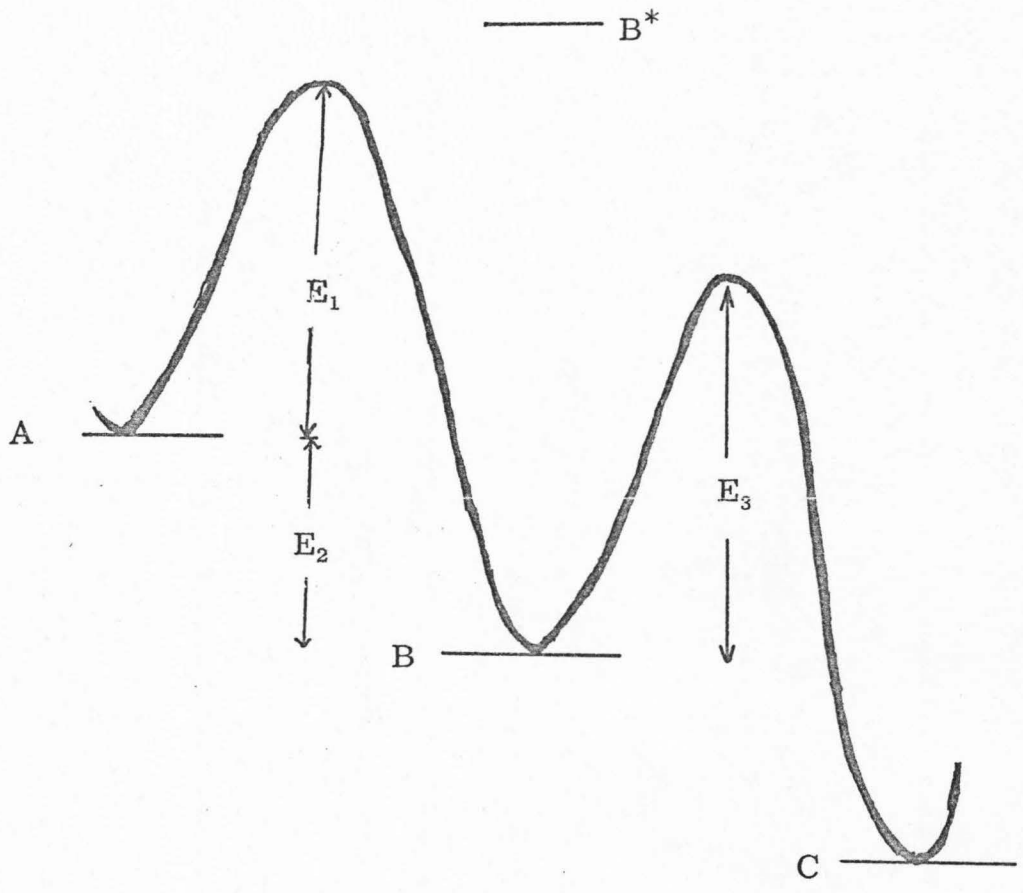


Figure 20. Energy Diagram for a Series of Exothermic Reactions

E is the total energy of B*, E_z is the zero point energy of B, E_z^+ is the zero point energy of the activated complex which goes to C, and s is the number of normal vibrational modes of B. The number of vibrational modes is important because one of the basic assumptions of the theory is that vibrational energy can flow freely throughout all of the vibrational modes. Reaction occurs only when a critical energy accumulates in the reactive mode. Therefore the more vibrational modes the smaller the probability that the energy of the excited species will accumulate in the reactive mode before collisional deactivation.

Results

Characterization of Products. The characterization of triene I was described in Chapter II. Fulvenallene (LV), ethynylcyclopentadiene (LVI), and heptafulvalene (LVII) were ultimately characterized by comparison of their spectral data with the data of published reports. Fulvanallene was characterized initially by its nmr, ir, and uv spectra. These were consistent with an ethylidene group fused to the 6 position of fulvene. Publication of the same spectral data by Hedaya (111) confirmed this assignment. Ethynylcyclopentadiene was identified from Hedaya's data also. The black residue left after distillation of the thermolysis reaction solution was inferred to be hydrocarbon in nature from its solubility in pentane and was characterized as heptafulvalene by comparison of its nmr with an nmr supplied by Professor W. M. Jones of authentic heptafulvalene. This product was only detected in preparative scale reactions

(yield less than 1%), and is not included in the results on the temperature and pressure dependences reported below. However a possible mode for its formation in the preparative reaction is presented in the discussion section.

Pressure and Temperature Dependence of the Product Ratios. In the vacuum flow system total pressure was varied by increasing the total amount of material passed through the tube or by addition of nitrogen prior to the transfer. The increase of material was achieved by dilution of trans-XVIII with n-hexane. The absolute pressure during the transfer was not determined but it seems safe to assume that up to a limit dependent upon the rate of vaporization of the mixture, the more of the mixture passed through the tube the greater will be the effective pressure. In order to confirm this, three runs were made in a static system where the absolute pressure could be measured by a McLeod gauge. The static system employed here was the same as that used in the kinetic experiments described earlier.

The results of pressure dependence studies at 420°, 460° and 520° in the vacuum flow system are presented in Table XV. The most important conclusions to be derived from these results are the following: (1) the initial observation that the relative yield of triene I increased with increasing pressure was substantiated; (2) for a given temperature the fulvenallene to ethynylcyclopentadiene ratio increased with increasing pressure; (3) the relative yield of triene at a given pressure decreased with increasing temperature; (4) the product ratios were independent of the surface

to volume ratio of the reactor.

The results of studies at 625° are recorded in Table XV. The trend towards lower relative yield at higher temperatures was maintained and also some new products were detected. At least ten new peaks were observed by glc, accounting for ~1% of the product mixture in the neat run but at least 26% of the product mixture in the run in hexane. In addition, the retention times of the new products are not the same in both cases. Glc-mass spectral analysis performed on the hexane product mixture indicated that the new products may be due to radical recombination reactions of hexane fragments with the C_7H_6 products. A peak at m/e 180 indicates that some dimerization took place.

In order to determine the thermal stability of I, LV, and LVI each was subjected to vacuum flow pyrolysis. The results listed in Table XVI show triene I to convert to LV and LVI at temperatures greater than 500°. Complete conversion takes place at 625°. Both the fulvene LV and the acetylene LVI were found not to interconvert under any conditions. At temperatures greater than 750° substantial losses of material and formation of uncondensable gases were noted. The ratio of LV to LVI from the pyrolysis of triene I is significantly higher than that obtained in the pyrolysis of trans-XVIII.

Experiments in the static system at 247° where the pressure could be measured absolutely gave the same kind of pressure dependence as the vacuum flow system. The relative yield of triene decreased from 100% at 70 torr to 92.7% at 1 torr to 70.5% at 0.1

torr (Table XVII). It appears that fulvenallene is not stable under the reaction conditions and that only the results in those runs of reaction time under 30 minutes represent accurate ratios of LV to LVI.

Table XV. Vacuum Flow Pyrolyses of trans-1,2-diethynylcyclopropane (XVIII)

Sample	Initial pressure (torr)	420° - 430° % reaction	Products % LVI	LV	I	LV/LVI
2 μl XVIII-t	0.02	73	8.6	19.5	71.9	2.27
1 μl XVIII-t/ 10 μl hexane	0.02	73	7.1	17.2	75.7	2.46
1 μl XVIII-t/ 50 μl hexane	0.02	65	4.6	11.5	84.0	2.41
1 μl XVIII-t/ 200 μl hexane	0.02	74	1.9	5.2	92.9	2.66
2 μl XVIII-t	0.10	96	5.8	13.9	80.3	2.41
1 μl XVIII-t/ 50 μl hexane	0.10	93	1.9	4.3	93.8	2.26
		455° - 465° [a]				
2 μl XVIII-t	0.02	95	15.5	30.5	54.0	1.97
1 μl XVIII-t/ 10 μl hexane	0.02	95	11.6	25.1	63.3	2.18
1 μl XVIII-t/ 50 μl hexane	0.02	95	7.2	17.5	75.3	2.42
1 μl XVIII-t/ 200 μl hexane	0.02	95	3.0	8.3	88.7	2.73

Table XV (cont'd)

2 μl XVIII-t	0.10	95	10.6	22.7	66.7	2.13
1 μl XVIII-t/ 50 μl hexane	0.10	95	3.7	9.8	86.4	2.62
		460° - 470°				
2 μl XVIII-t	0.02	95	16.0	32.0	52.0	1.98
1 μl XVIII-t/ 10 μl hexane	0.02	95	11.0	24.5	64.5	2.23
1 μl XVIII-t/ 50 μl hexane	0.02	95	7.6	18.1	74.3	2.39
1 μl XVIII-t/ 200 μl hexane	0.02	95	3.8	10.2	86.1	2.71
2 μl XVIII-t	0.10	95	10.6	22.4	67.0	2.11
1 μl XVIII-t/ 50 μl hexane	0.10	95	3.9	9.5	86.6	2.44
		510° - 520°				
2 μl XVIII-t	0.02	95	24.7	50.6	24.7	2.04
1 μl XVIII-t/ 10 μl hexane	0.02	95	18.4	41.9	39.7	2.28
1 μl XVIII-t/ 50 μl hexane	0.02	95	11.2	28.1	60.7	2.52
1 μl XVIII-t/ 200 μl hexane	0.02	95	9.1	25.2	65.7	2.80
1 μl XVIII-t/ 50 μl hexane	0.10	95	11.5	30.4	58.1	2.63

Table XV (cont'd)

		625° - 630°				Other products
5 μl XVIII-t	0.02	100	34.5	64.4	1.1	<1
.3 μl XVIII-t/ 50 μl hexane	0.02	100	21.8	50.8	1.1	26.3

[a] Pyrolysis in tube packed with segments of quartz tubing (surface to area ratio increased by a factor of 4.5).

Table XVI. Vacuum Flow Pyrolyses of Bicycloheptatriene (I), Fulvenallene (LV), and Ethynylcyclopentadiene (LVI)[a]

Temperature °C	Sample	Products %				
		LVI	LV	I	All others	LV/LVI
425	1 μl I/ 50 μl hexane	–	–	99	–	–
460	1 μl I/ 50 μl hexane	–	–	99	–	–
518	1 μl I/ 50 μl hexane	2.8	8.1	89.2	1	2.93
580	1 μl I/ 50 μl hexane	9.2	27.2	54.2	9.3	2.95
630	1 μl I/ 50 μl hexane	16.5	44.4	10.4	28.7	2.69
625	2 μl I	25.5	67.1	7.4	2.0	2.62
620	4 μl LV/ 50 μl hexane	–	96.	–	4	–
720	4 μl LV/ 30 μl hexane	1	90	–	10	–
620	3 μl LVI/ 30 μl hexane	100	–	–	–	–
720	3 μl LVI/ 30 μl hexane	99	<1	–	–	–

[a] Initial pressure was 0.02 torr in all cases.

Table XVII. Low Pressure Pyrolyses of trans-Diethynylcyclopropane in a Static Reactor

Pressure (torr)	Time in Reactor (min)	Conversion (%)	Products % LVI	LV	I	LV/LVI
1.0	30	75	2.4	4.9	92.7	2.03
0.15	50	75	10.3	12.9	76.9	1.26
0.10	10	25	9.6	19.9	70.5	2.07
0.10	20	56	9.7	18.6	71.7	2.01
0.10	40	75	11.0	15.9	73.1	1.44
0.10	60	71	14.6	16.5	68.9	1.13

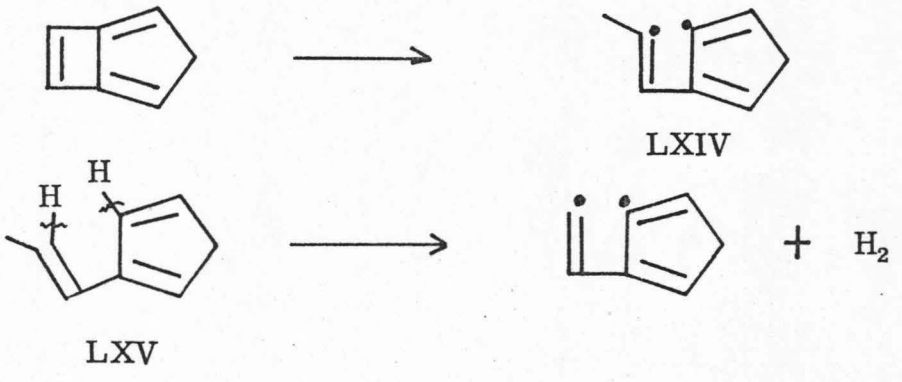
Discussion

The results from the vacuum flow system and especially from the low pressure static system experiments strongly implicate vibrationally excited triene I as an intermediate in these pyrolyses. More specifically it appears that triene I is formed with varying amounts of excitation and is deactivated to a certain extent before reaction to LV and LVI. These conclusions are discussed more thoroughly below.

Thermochemistry. The minimum amount of energy present in chemically activated I is equal to the sum of the activation energy for the trans-XVIII to I conversion and the difference between the heats of formation of I and trans-XVIII. The heats of formation of all the C_7H_6 species were estimated by the group additivity method of

Benson (112). The use of this method is quite straightforward but a knowledge of strain energies is necessary for accurate determinations of heats of formation. In the present case the strain energies of I and LV were not known and had to be estimated. The value for LV, estimated to be 10 kcal/mole, was based upon consideration of the known strain energies of cyclopentene (5.9 kcal/mole) and of cyclopentadiene (6.0 kcal/mole) (112). The addition of one more sp^2 center to the five membered ring should not increase the strain energy by more than 4 kcal/mole over these values. The estimation of strain energy of I was more difficult. Benson suggested a strain energy of 40 kcal/mole for I (113) from which a heat of formation of 81 kcal/mole is calculated. However the value calculated for LVI (89 kcal/mole) being 8 kcal/mole greater than the value for I requires that the conversion of I to LVI be endothermic. This is not consistent with the observation that I converts completely to LV and LVI at 625°. One expects most valence isomerizations which go to completion to be exothermic. (Although this generalization may not be strictly true for nonequilibrium situations the completeness of the reaction and the lack of conversion of LV or LVI to I implies it is true for the above case. Also, it is assumed that difference in ground state entropy are negligible for these rigid molecules.) Therefore the heat of formation of LVI is expected to be lower than that of I and accordingly triene I is assigned the value 92 kcal/mole. The strain energy for I is then 51 kcal/mole which is close to the value for cyclopropene (112).

Assignment of the activation energy of the trans-XVIII to I conversion was made from the results of the high pressure kinetics described earlier. The activation energy for the I to LV and LVI conversion may be estimated to be 55-60 kcal/mole from the reaction temperature in the vacuum flow system. An additional independent estimation of the energy of activation for the conversion of I to LV and LVI may be made from consideration of some preliminary results of Dr. T. J. Henry (114). There is evidence that the 1, 4-diradical is an intermediate in the pyrolysis of triene I (see below). Assuming that the rate determining step is breaking of the cyclobutene ring bond to give LXIV then the activation energy may be estimated from the difference in the heats of formation of I and LXIV. The heat of formation of LXIV was estimated from equation 2



LXIV

LXV

$$\Delta H_F^0(\text{LXIV}) = D(\text{vinyl C–H}) + D(\underline{\text{sec}}\text{-vinyl C–H}) + \Delta H_F^0(\text{LXV}) - D(\text{H–H}) \qquad (2)$$

The heat of formation of LXV was calculated to be 45.7 kcal/mole by the Benson method (112); D(vinyl C–H) was assigned the value 108 kcal/mole (strength of the C–H bond in ethylene (112)); D(sec-vinyl C–H) is estimated to be 104 kcal/mole; D(H–H) is 104 kcal/mole. From these values the heat of formation of LXIV is estimated to be 154 kcal/mole and the difference between the ΔH_f^o of I and ΔH_F^o of LXIV is 58 kcal/mole. This value represents the minimum activation energy for the conversion of I to LV and LVI. Assuming an activation energy of 5 kcal/mole for the closure of back to I (115) raises the estimation to 63 kcal/mole which is in good agreement with the value estimated from the pyrolysis experiments. The activation energy for the I to LV conversion is assumed to be 1 kcal/mole lower than that for the I to LVI conversion. This assignment is derived from the product ratio (3.0) of LV to LVI from the pyrolysis of triene I. All of the above values are summarized in the energy diagram given in Figure 21.

Pressure Dependence. From Figure 21 triene I is formed with at least 80 kcal/mole of energy over its ground state. The actual figure is probably higher due to extra vibrational energy in trans-XVIII before reaction. However the minimum amount is certainly enough to cause reaction to LV and LVI assuming the estimation of the activation energy for this process is reasonable.

In the vacuum flow system when more material is passed through the pyrolysis unit there are more molecule-molecule collisions which can remove excess vibrational energy from I, resulting in

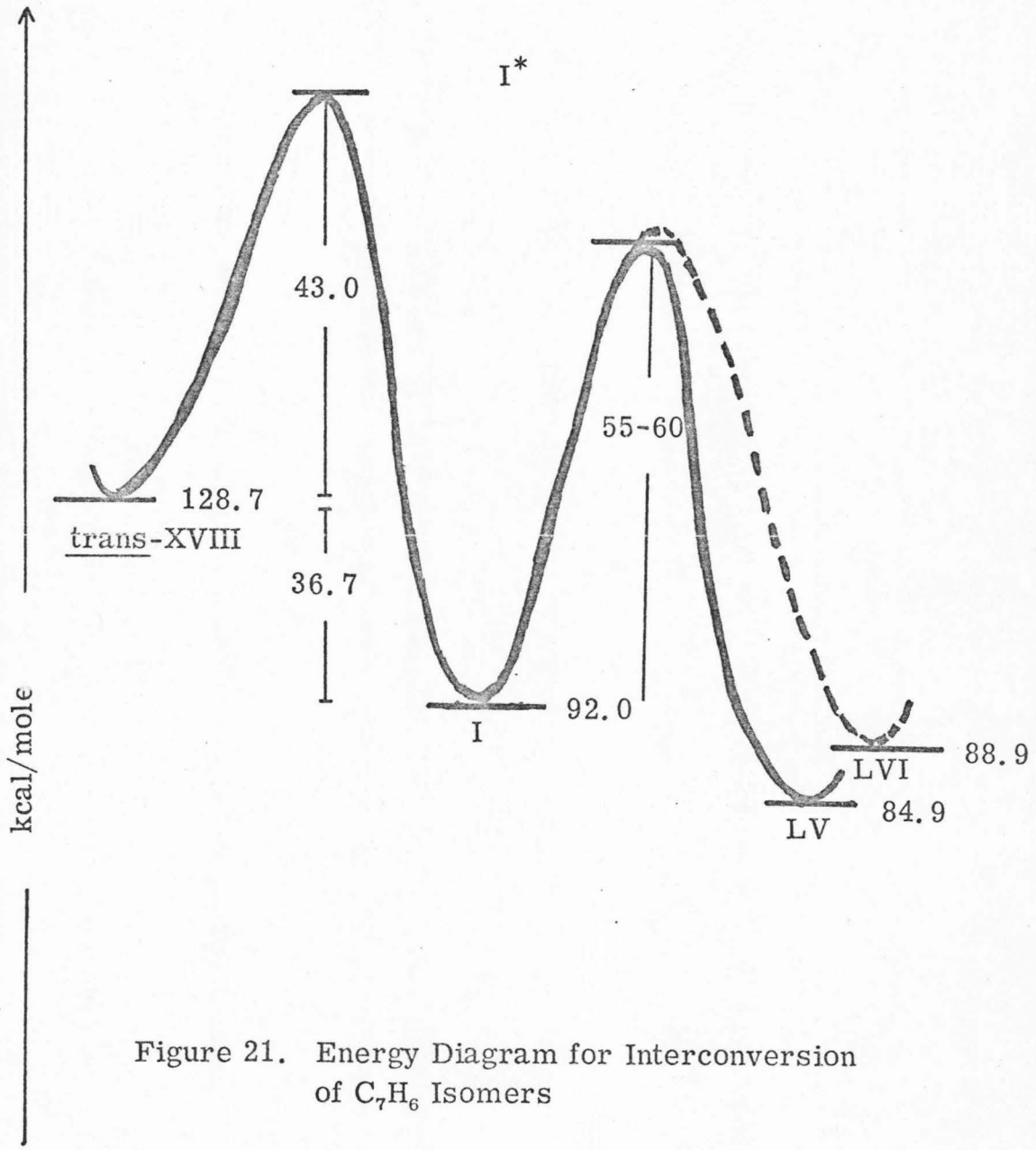
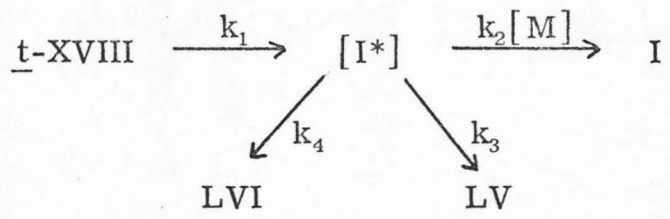


Figure 21. Energy Diagram for Interconversion of C_7H_6 Isomers

higher relative yield of triene. The vacuum flow system, although giving only semiquantitative results because of lack of absolute pressure measurements, does show the high sensitivity of the relative yield of triene I to changes in pressure. As such this unit is a very convenient means of testing for the intermediacy of chemically activated species in valence isomerizations.

More quantitative results from the static system enable one to test more rigorously for the intermediacy of vibrationally excited I (I*). A simple kinetic scheme for the formation of I, LV, and LVI in which I* is a reactive intermediate is given in Scheme 3. After making a steady state approximation for I* the kinetic equations may be solved (see Scheme 3) to give an expression which relates 1/P to D/S (ratio of decomposition products LV and LVI to stabilization product I). This expression requires that a plot of 1/P vs. D/S give a straight line. Observation of a straight line implies that the kinetic scheme is consistent with the observed results.

The plot of D/S vs. 1/P given in Figure 22 displays a reasonably good straight line although there is a small amount of scatter. Plots published by Frey (116) and Rabinovitch and Setser (110) for other systems show similar scatter even though the pressure measurements were quite accurate. The accuracy of pressure measurements in the present investigation is questionable because of the use of a McLeod gauge. The use of this gauge for condensable gases is not recommended. Taking into consideration the inaccuracy of the gauge, the results are certainly consistent with the intermediacy



$$\frac{d[I^*]}{dt} = k_1[\underline{t}\text{-XVIII}] - k_2[M][I^*] - k_3[I^*] - k_4[I^*]$$

steady state approximation $\quad \frac{d[I^*]}{dt} = 0$

then $\quad [I^*] = \frac{k_1[\underline{t}\text{-XVIII}]}{x}$

where $\quad x = k_2[M] + k_3 + k_4$

now $\quad \frac{d[I]}{dt} = k_2[M][I^*]$

$$= \frac{k_2[M]\, k_1[\underline{t}\text{-XVIII}]}{x}$$

similary $\quad \frac{d[LV]}{dt} = \frac{k_3 k_1[\underline{t}\text{-XVIII}]}{x}$

and $\quad \frac{d[LVI]}{x} = \frac{k_4 k_1[\underline{t}\text{-XVIII}]}{dt}$

then $\quad \frac{D}{s} = \frac{d[LV] + d[LVI]}{d[I]} = \frac{k_4 + k_3(k_1[\underline{t}\text{-XVIII}])}{k_2[M](k_1[\underline{t}\text{-XVIII}])}$

$$\frac{D}{s} = \frac{k_4 + k_3}{k_2[M]}$$

where $[M]$ is directly related to pressure (P).

Scheme 3

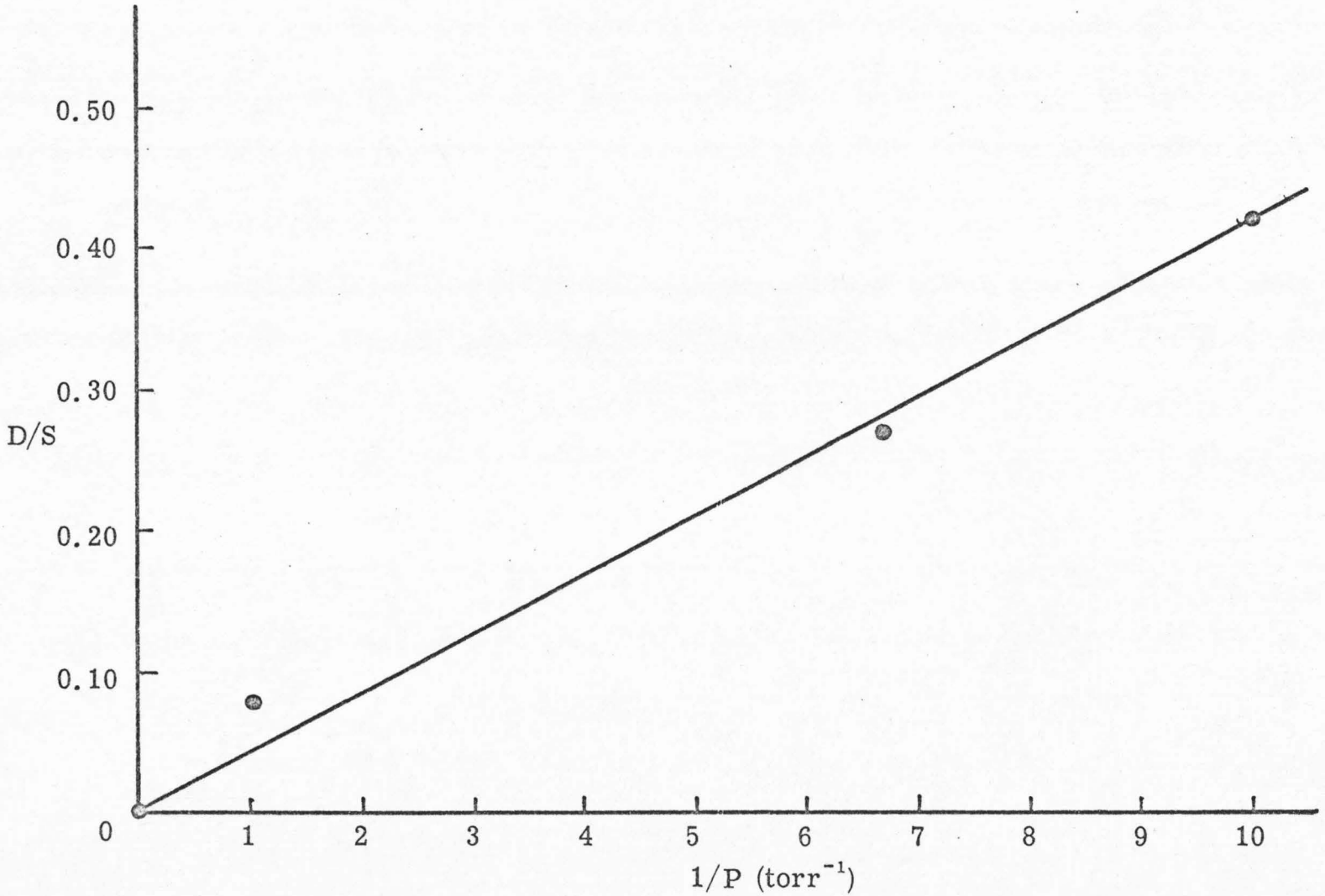


Figure 22. Ratio of the yield of LV and LVI to I as a function of the reciprocal of the total pressure

of chemically activated triene I* in the pyrolysis of trans-XVIII.

Rate of Reaction of I* to LV and LVI. The rate of reaction of I* to products may be estimated in two ways. For both cases it will be assumed that I* deactivates after every collision (this assumption is probably not very good for this system but is reasonable for an order of magnitude calculation). The first method relates the specific collision frequency (ω) to the rate of reaction of I* (k_{I*}). If products are to be observed at all k_{I*} must be equal to or greater than ω. Therefore a calculation of ω at a pressure and temperature at which LV and LVI are observed will give a lower limit to k_{I*}. The specific collision frequency may be calculated as below (117).

$$\omega = \frac{1693\ P\ (torr)}{\eta}\ sec^{-1}$$

where P(torr) = pressure in torr

and $$\eta = \frac{(\frac{5}{16\sigma^2})(\frac{kmT}{\pi})^{\frac{1}{2}}}{1+C/T}$$

where σ = molecular diameter

and C = Sunderland constant

Applying this equation to trans-XVIII where σ = 7Å, C = 700 (estimated from molecules of similar complexity (110) and T = 520° gives the values of ω listed below:

P(torr)	ω (sec^{-1})
70	2.2×10^9
1	3.4×10^7
0.1	3.4×10^6

Since the reaction products LV and LVI are observed at P = 1 and 0.1 torr the reaction rate of I* is probably 10^6 to 10^7 sec^{-1}.

The second and independent method for calculating k_{I*} is by application of the RRKM equation (Equation (1)). The relevant parameters here are $A = 10^{15}$ (a reasonable estimate for a transition state leading to cleavage of the cyclobutene ring of I); E = 80 kcal/mole and E_0 = 60 kcal/mole (see section on thermochemistry); E_Z = 73 kcal/mole (estimated by assuming 2.20 kcal per vibrational mode (110)); E_Z^+ = 65 kcal/mole (loss of vibrational modes upon bond breaking) and s = 33. For these values k_{I*} calculates to be $\sim 10^7$ sec^{-1}. This value is in very good agreement with that calculated from ω. In comparison Rabinovitch found the rate of reaction of activated cyclopropane to be 10^9 sec^{-1} for similar excitation energies. The difference in rate between I* and activated cyclopropane is probably due to the greater number of vibrational modes available to I into which excess energy may be transferred without reaction.

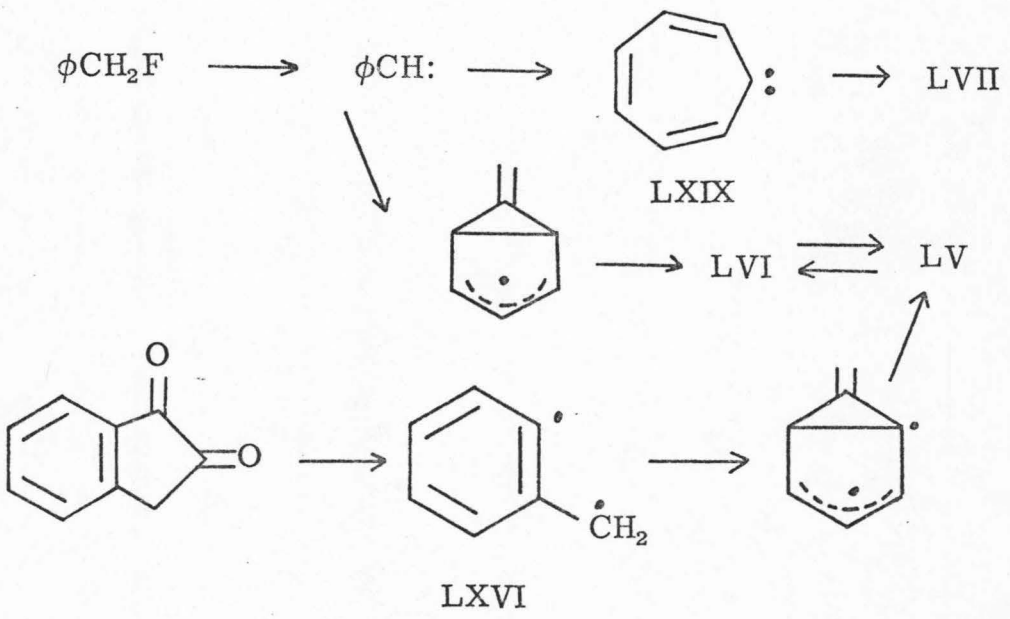
Temperature Dependence of Triene Yield. It was observed in the vacuum flow system that for a given pressure the relative yield of triene I was inversely proportional to temperature. Above 520° this may be rationalized by reaction of ground state triene I but at

420° and 470° another process must be operative. One reasonable explanation deals with excess vibrational energy present in trans-XVIII before reaction. It is reasonable to expect that the average amount of energy possessed by trans-XVIII before reaction at 420° will be less than that at 470°. After reaction then the excited triene will also possess a different amount of energy depending upon the temperature. RRKM theory predicts that other things being equal the greater the total amount of energy possessed by the reactant the faster will be the reaction. In terms of the RRKM equation since E_{470} is greater than E_{420} then k_{470} will be greater than k_{420}. Therefore, since triene I will react faster at 470° it will have less chance to deactivate by collision resulting in lower yields.

Pressure Dependence of the Fulvenallene to Ethynylcyclopentadiene Ratio. The pressure dependence of the LV/LVI ratio is another aspect of the reaction of triene I with different amounts of excitation. At higher pressures triene I* has more of a chance to lose energy by collision. The energy loss has been shown by Rabinovitch (118) to be stepwise for other cases. If the same applies here then at higher pressures the reactive triene molecules will be on the whole less excited just prior to reaction than at lower pressures. The change in the ratio may be rationalized by reference to Equation (1). The rates for both the triene to LV and the triene to LVI transformations are described by this equation. The form of equation is such that at higher values of E differences in rates for different processes will be attenuated. Thus if the rates become

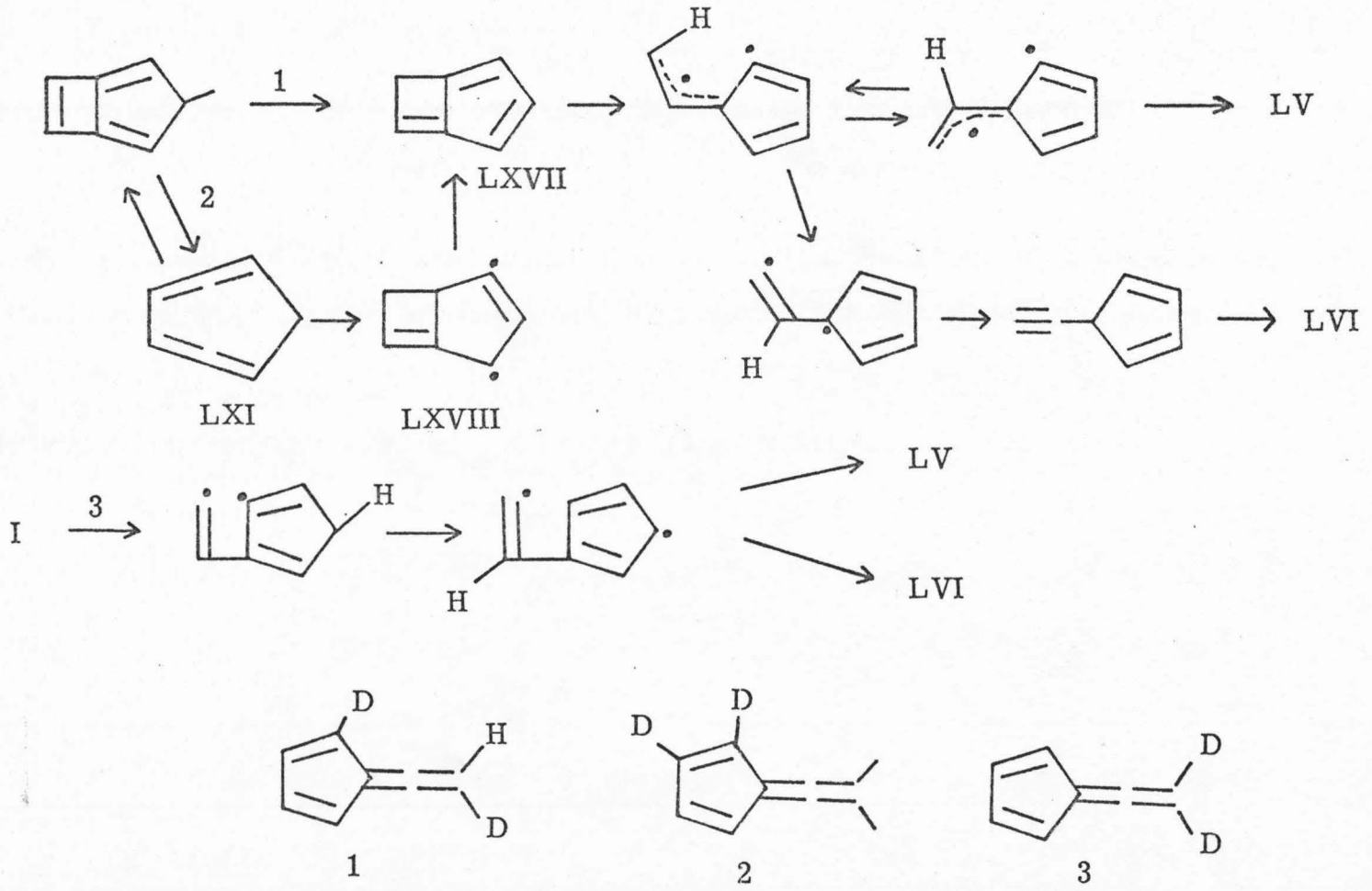
closer at higher energies then the ratio of LV to LVI should become closer to one. This behavior is observed. The ratio at 470° changes from three to one to two to one as the pressure is decreased. Triene I pyrolyzed by itself gives a ratio of three to one at low conversion to LV and LVI. Presumably this represents the reaction of triene with little extra energy and the ratio is the same as that observed when trans-XVIII is pyrolyzed at higher pressures. Increases in temperature should also give the same behavior and indeed at 420° the change in the ratio with pressure is not nearly as much as at 470°.

Possible Mechanisms of Product Formation. The mechanisms of the formation of LV, LVI, and LVII are open to much speculation. These species have previously been isolated by Hedaya from the flash vacuum pyrolysis of benzyl fluoride or 1, 2-indandione (111). The initial product from the former reaction is phenyl carbene while in the latter case it is the diradical LXVI. Further transformation of these reactive species give LV and LVI. In each case the formation of LV is depicted as arising from isomerization of LVI or vice versa. However in the present results control experiments showed LV and LVI not to be interconverting under the reaction conditions or at even much higher temperatures. Recently, Dr. Hedaya has communicated to us that the isomerization reaction between LV and LVI takes place only in a packed reaction vessel. This strongly implies that the reaction is surface catalyzed and that for the present system each compound is being formed separately.



LXVI

Three mechanisms can be proposed which are consistent with the independent formation of LV and LVI (Scheme 4). The first step in mechanism 1 is a Woodward-Hoffmann allowed 1, 5-hydrogen shift. This type of shift takes place quite readily in cycloheptatriene where the preferred buckled conformation of this molecule greatly facilitates the hydrogen shift (120). Of course in the case of I the geometry is not nearly so favorable and this may be the cause of the relatively high activation energy for the formation of LV and LVI. The very highly strained fulvene LXVII resulting from the initial hydrogen shift may then rearrange to LV and LVI by a series of bondbreakings and hydrogen shifts. Mechanism 2 includes 1, 5 ring closure of diallene LXI to give LXVIII, followed by a 1,2 hydrogen shift to



Scheme 4

give the same fulvene as in mechanism 1. Mechanism 3 requires cleavage of the 1, 7-cyclobutenyl single bond followed by the indicated hydrogen shifts to give LV and LVI. The three mechanisms may be distinguished experimentally by deuterium tracer techniques. The different dideuterofulvenallenes resulting from rearrangement of 6, 7-dideutero-I are given at the bottom of Scheme 4. Some preliminary results obtained by Dr. T. J. Henry (114) indicate that mechanism 3 may obtain for this rearrangement.

Hedaya observed substantial amounts of heptafulvalene in the pyrolysis of benzyl fluoride (111). He postulated the intermediacy and subsequent dimerization (119) of tropyl carbene (LXIX) to account for this observation. In the present case there are two conceivable mechanisms which can account for the formation of LVII. The first includes rearrangement of I to LXIX by a 1, 3 hydrogen shift and subsequent dimerization. The second involves the intermediacy of Breslow's triene II. The dimers III and IV of II may rearrange in a 10 electron process to give LVII. The relative merits of these mechanisms await further proof. Conceivably the second could be tested by subjecting dimers III and IV to the reaction conditions. Although this experiment was not performed it was found that the dimers are stable to 350° in the injection port of a Hewlett-Packard glc. However further work at higher temperature is needed here.

CHAPTER VI
EXPERIMENTAL

General

Pentane was purified by stirring over concentrated sulfuric acid and aqueous potassium permanganate in succession. After washing with saturated sodium bicarbonate solution and drying, pentane was distilled through a 24" tantalum wire column. The fraction boiling at 35° was collected. Tetrahydrofuran was dried by distillation from lithium aluminum hydride. All boiling points and melting points are uncorrected. Infrared (ir) spectra were determined on a Perkin-Elmer IR 257 instrument as carbon tetrachloride solutions unless otherwise noted. Ultraviolet spectra (uv) were obtained on a Cary Model 14 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were determined on Varian A60-A, A56/60 and 220 MHz instruments. Unless otherwise noted carbon tetrachloride is the solvent. All shifts are referenced to internal tetramethylsilane. Mass spectra (ms) were determined on either a CEC-21-103C instrument at 10μ an ionizing current and 70 v electron energy or on an EAI Quad 300 Mass Spectrometer interphased with a Hewlett-Packard Research Gas Chromatograph. Qualitative and preparative gas chromatography (glc) was carried out on Varian Aerograph 90-P3 instruments. Quantitative analytical work was done on a Hewlett-Packard 5750 (flame ionization detector) Gas

Chromatograph equipped with a Disc 607 integrator or a Hewlett-Packard 3370A Digital integrator. The following columns were used: column A - 6' × 1/4" aluminum, 20% Se 30 on Chrom P; column B - 10' × 1/4" aluminum, 20% Carbowax 20 M on Chrom P; column C - 10' × 1/4" aluminum, 10% UCW98 on Chrom P; column D - 5' × 1/4" aluminum, 8% UCW98 on Chrom P; column E - 12' × 1/4" aluminum, 8% Se 30 on Chrom P; column F - 10' ×1/4" glass, 8% Se 30 on Chrom W aw-dmsc; Column G - 10' × 3/8" glass, 20% UCW98 on Chrom W aw-dmsc; column H - 10' × 1/8" stainless steel, 8% UCW98 on Chrom W aw-dmsc; column I - 10' × 1/4" aluminum 20% Se 30 on Chrom P. For 1/4" and 3/8" columns mesh size was 60-80; for 1/8" column mesh was 100-120. Flow rate was 60 ml/min for 1/4" and 3/8" columns and 20 ml/min for the 1/8" column.

Reaction of XXXVI with Zinc and Acetic Acid (121)

The dichlorocyclopropane XXXVI was prepared by the method of Cadiot and Vo-Quang (122). A mixture of 0.70 g of acid-washed zinc, 4 ml of glacial acetic acid, 3 ml of ether and 1.5 g (0.01 m) of XXXVI was refluxed for 48 hr in a 25 ml single-necked flask. The black reaction mixture was diluted with water and extracted with ether. The yellow ether solution was washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Glc analysis (column A at 60°) showed, other than that due to starting material, 4 major peaks of which the largest constituted 40% of the total peak area. This material, isolated by preparative glc, was

identified as 1-acetyl-1-methyl-2, 2-dichlorocyclopropane by comparison of its nmr with that reported by Vo-Quang (123): nmr τ 7.73 singlet (3H); 7.80 doublet (1H); 8.40 singlet (3H); 8.78 doublet (1H).

Reaction of XXXVI with Lithium in t-Butanol (124)

To a stirred solution of 15 ml of dry tetrahydrofuran (THF) and 2.3 g (0.015 m) of XXXVI in a 100 ml flask was added small pieces of lithium (1.6 g (0.23 m) total) and t-butanol at such a rate that the temperature of the reaction mixture did not exceed 40°. After the addition was complete, the mixture was allowed to stir for 1 hr and added to ice water. The aqueous mixture was extracted with pentane and the pentane washed with water until no more THF or t-butanol was present. Glc analysis (column β at 130°) showed at least 14 new peaks, the last being the major peak. This peak was collected and gave the following spectral data: ir 3295, 3040, 2120, 930 cm^{-1}; nmr τ 7.12 triplet (1H); 8.05 singlet (1H); 8.69 singlet (3H); 8.89 doublet (2H). From the nmr data this compound is identified as trans-1-methyl-2-chloro-1-ethynylcyclopropane. The spectrum published of the trans-bromo compound is similar to that above (123).

Analysis calc. for C_6H_7Cl: C 62.88%, H 6.11%, Cl 31.01%; found: C 63.23%, H 6.17%, Cl 31.08%.

Reaction of XXXVII with Tri-n-butyltin Hydride

The dibromocyclopropane XXXVII was prepared by the method

of Cadiot and Vo-Quang (122) and tri-n-butyltin hydride was prepared by the method of Van der Kerk (125). The dibromo compound XXXVII was contaminated by ~20% bromoform. To 6.0 g of XXXVII in a 3-necked 50 ml flask equipped with a dropping funnel, reflux condenser and magnetic spinbar was added under nitrogen 14.7 g of tri-n-butyltin hydride. After stirring overnight at room temperature volatile material was distilled at 30°/25 mm and condensed in a dry ice trap. Nmr analysis showed the volatile material to be methyl bromide. Distillation at 30°/1 mm gave 1.1 g of the isomeric monobromides. To 1 g of the monobromides was added 1.8 g of tri-n-butyltin hydride at 0° under nitrogen. The mixture was stirred at 25° for three days. Distillation at 25°/25 mm gave 0.15 g of 1-methyl-1-ethynylcyclopropane (XXXV): ir 3300, 3080, 2110, 900 cm^{-1}; nmr τ 8.32 singlet (1H); 8.75 singlet (3H); 9.0-9.6 complex multiplet (4H).

3-Methyl-3-ethynyl-Δ^1-pyrazoline (XXXVIII)

To about 1.5 g (0.036 m) of diazomethane in ether was added 2.0 g (0.03 m) of 2-methyl-1-buten-3-yne (XXXIV). The mixture was let stand in a sealed, dark bottle for four days. By this time the solution was colorless. Distillation of the ether at 25°/50 mm left 1.86 g of a clear viscous oil which from the nmr is a 50:50 mixture of XXXVIII and 3-(1-methylvinyl)-pyrazole (126). Distillation of this mixture at 25°/1 mm gave about 0.2 g of XXXVIII: ir 3300, 2110, 1550 cm^{-1}; nmr (neat) τ 5.80 triplet (2H); 7.47 singlet (1H); 8.3-8.7 complex multiplet (2H); 8.82 singlet (3H).

Analysis calc. for $C_6H_8N_2$: C 66.67%, H 7.41%, N 25.92%; found: C 64.62%, H 7.10%, N 27.18%.

Distillation 40°/1 mm gave 1 g of a mixture of pyrazole and pyrazoline. Knowing the spectra of the relatively pure pyrazoline it was possible to determine the spectra of the pyrazole: ir 3300-3000, 1635 cm^{-1}; nmr (neat) τ 3.0 doublet (1H); 4.15 doublet (1H); 5.0 singlet (1H); 5.50 multiplet (1H); 8.40 doublet (3H); -1.2 singlet (1H).

Pyrolysis of XXXVIII. Pyrolysis was carried out at 120-135° on 0.1 g of XXXVIII until nitrogen evolution stopped. All volatile materials were collected at -78°. Except for minor impurities the decomposition product was identical to 1-methyl-1-ethynylcyclopropane with respect to nmr and ir spectra. The decomposition appeared to be quantitative.

Reaction of Diazomethane with 1,5-Hexadiyn-3-ene (XXXI)

An ethereal solution of XXXI (~2.0 g) was prepared by the method of Sondheimer et al. (127). To this solution was added a solution of 1.5 g of diazomethane in 40 ml of ether. The mixture was sealed in a dark bottle and stored at 10° for three days. Flash evaporation of the resultant yellow solution left ~0.75 g of a red viscous oil which turned darker upon exposure to air. Glc and tlc analysis showed this mixture to be very complex. Heating ~0.1 g of this material to 130° resulted in production of very little nitrogen.

Propargylamine (30)

A 500 ml single-necked round bottomed flask equipped with distilling head and water condenser was charged with 74 g (0.69 m) of benzylamine and 61 g (0.33 m) of N-propargylphthalimide. The mixture was brought to 130 and all material boiling between 85 and 90 was collected. The yield of propargylamine was 16.4 g (89.5% of theoretical yield). Nmr (neat) 6.62 (2H) doublet J = 2.5 Hz; 7.40 (1H) triplet J = 2.5 Hz; 8.08 (2H) singlet.

Propargylurea (128)

A 250 ml, 3-necked round bottomed flask equipped with magnetic stirrer, reflux condenser and dropping funnel was charged with 22.0 g (0.393 m) of propargylamine. Stirring was initiated and the amine brought to 0° as cold 27% hydrochloric acid was added dropwise until the contents of the flask were slightly acidic. After bringing the pH of the mixture to 6 with dilute potassium hydroxide solution, 38 g (0.47 m) of potassium cyanate was added. The mixture was heated on a steam bath until solution took place. After cooling to 0° the white crystalline precipitate was suction filtered, washed with cold water and dried in vacuo over phosphorous pentoxide. The yield of propargylurea is 31.5 g (82%); mp 126.5-128° (lit. 128-129° (127)); ir (mull) 3440, 3350, 3280, 1650, 1600 cm^{-1}; nmr ($(CD_3)_2CO$) τ 4.68 (broad s) 1H, 6.20(d) 2H, J = 2.5 Hz; 7.01(s) 2H, 7.53(t) 1H J = 2.5 Hz.

N-Nitroso-N-propargylurea

The general procedure of Werner was used (129). To a 500 ml beaker containing 4.50 g (0.046 m) or propargylurea and 6.4 g (0.092 m) of sodium nitrite in 90 ml of water at 5° was added a cold solution of 4.5 g of sulfuric acid in 23 ml of water over one hour. After stirring for two hr at 5°, the entire mixture was extracted with ether, washed with brine and dried over anhydrous sodium sulfate. Distillation of the ether at 25°/50 mm left 3.53 g (60%) of N-nitroso-N-propargylurea mp 69-70° after one recrystallization from water: ir ($CHCl_3$) 3530, 3490, 3410, 1790, 1575, 1510 cm^{-1}; nmr ($CDCl_3$) τ 3.0-4.0 broad singlet (2H); 5.52 doublet (2H) J = 2.5 Hz; 7.98 triplet (2H) J = 2.5 Hz.

Diazopropyne (XL)

The method of Gramas (30) was used. To a solution of 1.0 g of sodium hydroxide, 5.0 g of $Na_2HPO_4 \cdot 7H_2O$, in 60 ml of water and 50 ml of diethyl ether or pentane at 0° was added dropwise a solution of 4 g (0.036 m) of N-nitroso-N-propargylurea in 100 ml water. After addition was complete the orange mixture was stirred at 0° for one hr. The aqueous layer was pipetted from the orange ethereal layer which was decanted into a flask and cooled to -78° to precipitate water. After filtration through glass wool a deep orange solution of diazopropyne was obtained. If the organic layer was pentane the cooling step was omitted.

The yield of diazopropyne appeared to be higher in ether (40%) than in pentane (25%). It was characterized by reaction with 2N hydrochloric acid to give propargyl alcohol. Ir XL (pentane) 3320, 2125, 2075 cm^{-1}.

1-Methyl-1, 2-diethynylcyclopropane (XLI)

A mixture of 12 ml of eneyne XXXIV and the above diazopropyne solution was photolyzed at 0° until nitrogen evolution ceased. A Hanovia medium pressure lamp inside a pyrex well was the light source. The cloudy solution was filtered and distilled at 25°/2 mm into a dry ice trap. After concentration to 3 ml through a 12" Vigreaux column under nitrogen, the diacetylene XLI was separated from solvent by preparative glc (column C at 120°, rt 9 min). Collected were ~100 mg (3% from nitrosopropargylurea) of XLI: ir 3300, 3090, 3010, 2980, 2940, 2130, 1460, 1448, 1385, 1300, 1248, 1215, 1115, 1080, 1050, 978, 945, 929, 840 cm^{-1}; nmr (220 MHz) τ 8.18 (d) (1H) J = 2 Hz; 8.23 (s) (1H); 8.30 (t) (1H) J = 9, 6, 2 Hz; 8.58 (s) (3H); 8.73 doublet of doublet (1H) J= 9, 4Hz; 9.25 (t) (1H) J = 6, 4.5 Hz; m/e (70 v) 104 (11), 103 (100), 78 (72), 51 (46); uv, only end absorption.

Analysis calc. for C_8H_8: C 92.26%, H 7.74%; found: C 92.07 %, H 7.94%.

2-Methylbicyclo[3.2.0]hepta-1, 4, 6-triene (LIV)

A mixture of 85 mg of the diyne XLI and 1 ml of carbon tetrachloride was vaporized by a nitrogen flow of 60 ml/min through a 25 × 1.5 cm pyrex tube heated to 350° by an open tubular oven into a trap held at -25° by a CCl_4 slush bath. Glc analysis (column C at 100°) of the condensate showed no peak due to XLI. Spectral analysis were performed on the condensate: ir 3090, 3070, 2970, 2915, 2880, 1675, 1440, 1425, 1415, 1283, 1120, 1082, 930, 900 cm^{-1}; nmr 3.21 m (1H); 3.33 m (1H); 4.97 m (1H); 6.72 m (2H); 8.22 m (3H) (all absorptions exhibited fine splitting).

Triene LIV was obtained in pure form by preparative glc (column C at 100°): uv (cyclohexane) λ_{max} 204 (log ϵ = 4.15), 277 (log ϵ = 3.3) nm; m/e (70 v) 104 (95), 103 (96), 73 (100). The yield of LIV was estimated to be 30-40%.

Reaction of Propargyl Bromide and 2-Methyl-1-buten-3-yne with Potassium t-Butoxide

A dry 3-necked, 25 ml round bottomed flask fitted with a nitrogen inlet, thermometer, magnetic spin bar, and dropping funnel was charged with 1.98 g (0.030 m) 2-methyl-1-buten-3-yne and 10 ml pentane. After bringing the temperature of the contents of the flask to -20° with a dry ice acetone mixture, 1.25 (0.011 m) of potassium t-butoxide was added with stirring. Propargyl bromide (1.19 g; 0.010 m) was added dropwise to this mixture over 35 min, a little pentane added from time to time to facilitate stirring. After addition

was complete no more dry ice was added to the cooling bath so that the mixture was allowed to come to 5° slowly. At this temperature the dark orange mixture was added to 60 ml of water, the pentane layer separated, washed with water and dried over sodium sulfate. The orange pentane solution was flash distilled at 25°/1 mm into a dry ice trap. The pentane was distilled off through a 12" Vigreaux column and the residue analyzed by VPC (column D at 80°). Analysis showed the presence of 4 peaks, a major peak at rt 3.5 min accounting for 80% of the peak area. Addition of authentic 1-methyl-1,2-diethynylcyclopropane to the residue and subsequent vpc analysis showed this peak not to be due to the diacetylene. This new material isolated by preparative glc (column E at 120°) weighed 0.203 g. Nmr analysis (τ 6.04 doublet 2H; 7.82 triplet 1H; 8.82 singlet 9H) of this substance is consistent with that expected for propargyl t-butyl ether. The yield of this ether is 18%. A repeat of this reaction at -50° and -20° gave the same results.

Reaction of Propargyl Bromide and 2-Methyl-1-buten-3-yne with Methyl Lithium

Into a 25 ml flask equipped as above and containing 1.19 g (0.01 m) of propargyl bromide and 2 ml dry ether at -50° was added 5 ml of 2.04 M ethereal methyl lithium (0.01 m). After stirring for 5 min 1.5 g (0.023 m) of the eneyne was added and the mixture allowed to come to room temperature over 2.5 hr. About 15 ml of water was added and the ethereal phase separated. The aqueous

layer was extracted once with 5 ml of ether and the combined ether layers washed with brine and dried over anhydrous sodium sulfate. Vpc analysis of the combined layers showed no trace of the diethynylcyclopropane.

A repeat of this reaction in which methyllithium was added to the enyne and the bromide was unsuccessful.

Reaction of Chloromethylcyclopropylketone with Triethyl Phosphite

Chloromethylcyclopropylketone was prepared by the method of Hanack (35). A 10 ml 1-necked flask was charged with 0.7 g (0.0042 m) of triethyl phosphite, 0.5 g (0.0042 m) of chloromethylcyclopropylketone and 1 ml ethanol. The flask was fitted with a reflux condenser, the top of which was connected to a dry ice trap. The mixture was brought to reflux and after 19 hr glc analysis (column A at 160°) showed the presence of two new peaks at 10 min and 17 min. Peaks due to starting material had decreased by 90%. The mixture was cooled and the ethanol removed by flash distillation leaving 0.62 g of a light yellow oil. Nmr analysis of this mixture gave absorptions which were attributed to enol phosphate XLV and ketophosphonate XLVI by comparison with nmr spectra of similar compounds (see Chapter II). From the nmr integrations it appears that the relative yield of each is 50%. The overall yield is 66%. Partial nmr XLV: τ 5.27 (t) J = 2 Hz; 5.53 (t) J = 2 Hz (vinylic protons); XLVI: τ 6.81 (d) J = 22.5 Hz (proton α to phosphorous). A small amount of volatile material condensed in the dry ice traps and is probably ethyl

chloride.

Reaction of the Mixture of XLV and XLVI with Bases

1. Reaction with potassium t-butoxide. A three-necked 25 ml flask fitted with a reflux condenser, the top of which was connected to a water aspirator through a dry ice trap and drying tube, and a magnetic spin bar was charged with 0.254 g (0.0023 m) of potassium t-butoxide, 0.50 g (0.0023 m) of the mixture of XLV and XLVI and 2 ml of DMSO. As the mixture was stirred the pressure of the system was brought to 100 mm by means of the water aspirator. After 45 min no material had collected in the dry ice trap. The dark red mixture was added to pentane-water and the organic layer washed and analyzed by glc (column B at 80°). Three new peaks at rt 3.6, 4.2 and 13.3 min were found. In order to test for the presence of cyclopropylacetylene, this substance was prepared by the reaction of 0.014 g of potassium t-butoxide and 0.025 g of 1,1-iodo-cyclopropylethylene in 1 ml of DMSO and subsequent isolation as a pentane solution (36). A portion of the pentane solution was added to the pentane solution from the phosphate reaction and the mixture analyzed by glc. The same three peaks were observed. It appeared from this result that cyclopropylacetylene was formed in the phosphate reaction. However a repeat of this experiment failed to reproduce this result. Also, a similar experiment in which 0.011 g of potassium t-butoxide, 0.022 g of the phosphate mixture and 1 ml of pentane-ether were allowed to stir for 1 hr gave none of the acetylene by glc

analysis.

2. Reaction with sodamide. To a single-necked 10 ml flask equipped with magnetic spin bar and soda lime drying tube was added 0.008 g sodamide, 1 ml dry ether and 0.022 g of the XLV-XLVI mixture. The mixture was stirred at room temperature for 2.5 hr. Aliquots were taken at 5, 30, 90, and 150 min; analysis of these by glc (column B at 80-90°) showed the presence of only one new peak at rt 11-15 min which is tentatively identified as cyclopropylmethyl-ketone by spiking experiments. No peak due to cyclopropylacetylene was observed.

Very similar experiments in which lithium diisopropylamide and diazabicyclononene (DBN) were substituted for sodamide gave no products.

3. Reaction with sodium ethoxide. A mixture of 0.0023 g of sodium ethoxide and 1 ml of absolute ethanol was placed in a 10 ml single-necked flask equipped with a reflux condenser and a calcium sulfate drying tube. After bringing the mixture to reflux 0.022 g of the XLV-XLVI mixture was added and the course of the reaction followed by analysis of aliquots by glc (column B at 90°). Over 1.5 hr only two product peaks at rt 3.9 and 10.9 were observed. The latter is due to cyclopropylmethyl ketone but the former is not due to cyclopropylacetylene.

trans-Diacetylcyclopropane (XLVIII)

A 3-necked 1000 ml round bottomed flask equipped with a mechanical stirrer, nitrogen inlet, Gooch tube, thermometer, and cooling bath was charged with 125 g (1.36 m) of chloroacetone and 201 g (2.88 m) of methylvinylketone. Nitrogen was passed over this mixture and the cooling bath was charged with an ice-water mixture. After the contents of the flask had come to 0°, 75 g (1.34 m) of pellet potassium hydroxide was added via the Gooch tube at such a rate to keep the temperature below 5° (about 2.5 hr). During the course of the addition the mixture turned bright orange and cloudy and at times became very viscous. Small amounts of ether (~50 ml) were added from time to time to facilitate stirring. After addition was complete the mixture was allowed to stir for 0.5 hr and poured into 1000 ml of water and the resultant mixture extracted with 3-200 ml portions of ether. The combined ether layers were washed with water and brine and dried over anhydrous sodium sulfate. Distillation of the ether at 25°/50 mm left 250 g of a very viscous, syrupy, yellow oil. Distillation at 100° oil bath temperature and 0.2 mm gave 90 g of a water white liquid. This liquid, consisting of 70-80% of XLVIII and 20-30% of ether and methylvinylketone, was subjected to fractional distillation through a 12" vacuum jacketed Vigreaux column. The fraction boiling at 98°/25 mm weighed 63.7 g and is greater than 90% pure trans-diacetylcyclopropane (XLVIII) (yield ~38%). For spectral and combustion analysis, pure XLVIII was isolated by preparative

glc (column F at 90°; rt 5 min): ir 3000, 2965, 2915, 1700, 1425, 1400, 1360, 1325, 1175, 975, 890 cm^{-1}; nmr τ 7.64 apparent triplet (2H), J = 7.0 Hz, cyclopropyl protons α to the carbonyl groups; 7.76 singlet (6H), methyl protons; 8.72 apparent triplet (2H), J = 7.0 Hz, cyclopropyl protons α to carbonyl groups.

Analysis calc. for $C_7H_{10}O_2$: C 66.64%, H 7.99%; found: C 66.56%, H 7.88%.

Two additional experiments were performed in an attempt to increase the yield of XLVIII.

1. The apparatus described above (except for the Gooch tube) was charged with 124 g of chloroacetone, 194 g of methylvinylketone and 100 ml of water. After bringing the mixture to 0° a solution of 75 g of potassium hydroxide in 200 ml of water was added over three hr. The reaction mixture, treated as above, yielded 98 g of clear liquid separated from polymeric material by distillation at 25°/1 mm. Glc analysis showed the presence of at least three peaks of which the one due to XLVIII accounted for 70% of the total peak area. This liquid gave three fractions upon distillation: A. 5 g boiling at 25°/6 mm; B. 51 g boiling at 75-80°/10 mm; C. 30 g boiling at 90°/5 mm. Fraction B consists of 90-95% pure XLVIII (~30%); ir analysis of fraction C showed broad hydroxylic absorption at 3500-3200 cm^{-1}.

2. A 3-necked 25 ml flask equipped with a magnetic spin bar, dropping funnel and argon inlet was charged with 1.23 g (0.0133 m) of chloroacetone, 1.90 g (0.0271 m) of methylvinylketone and 2 ml of

methanol. After bringing the contents of the flask to 0°, a solution of 0.74 g (0.0132 m) of potassium hydroxide in 2 ml of methanol was added dropwise over 5 min. After addition was complete the mixture was allowed to stir for 15 min and then added to 5 ml of water and the resultant mixture extracted with 3-10 ml portions of ether. After washing and drying over anhydrous sodium sulfate ether was removed from the mixture by distillation at 30°/50 mm leaving 1.5 g of a yellow oily residue. Distillation of this material at 30°/0.05 mm gave 1.36 g (~90%) of 4-methoxybutan-2-one which was identified from an nmr of a sample purified by preparative glc (column F at 90°, rt 3 min): nmr τ 6.45 triplet (2H), J = 6 Hz methylene, protons α to methoxy; 6.78 singlet (3H), methoxy protons; 7.43 triplet (2H), J = 6 Hz, methylene protons α to carbonyl; 7.91 singlet (3H), methyl protons α to carbonyl.

Chlorides XLIX, L, and LI

To a 2000 ml, 3-necked flask equipped with mechanical stirrer, dropping funnel, reflux condenser, and argon inlet was added 210 g (1.01 m) of phosphorous pentachloride. After flushing the system with argon, 1000 ml of anhydrous ether was added slowly for the first 100 ml then more rapidly to the pentachloride. To the resultant yellow slurry was added dropwise over 1 hr a solution of 63 g (0.50 m) of dione XLVIII in 40 ml of anhydrous ether. Gentle refluxing of the ether took place over the course of the addition. The progress of the reaction was monitored by glc (column F at 105°), the peaks of

interest having retention times 3.7 min (dione XLVIII), 4.4 min (dichloride XLIX), 7.8 min (trichloride L), 14.3 min (tetrachloride LI). After 2 hr stirring the bulk of the pentachloride had reacted. However, glc analysis showed the dione XLVIII still to be present. Accordingly phosphorous pentachloride was added in 10 g portions until 95% of the dione had reacted and until no further enhancement of product peaks was observed. The total amount of the pentachloride added was 260 g (1.25 m) and completion of the reaction took 3.5 hr. The resultant orange-red solution was cautiously added portionwise to a large excess of ice water with vigorous stirring. The cold aqueous mixtures were extracted with ether and the combined ether extracts were washed with saturated sodium bicarbonate solution until the aqueous layer remained basic. After washing with water and brine, the yellow ether solutions were dried over anhydrous magnesium sulfate. Removal of the ether by distillation at 25°/50 mm left 69 g of a yellow oil. Distillation of this material at 20-40°/0.08 mm gave 57.7 g of a light green oil. It was ascertained by glc analysis that chlorides XLIX, L, and LI comprised ~77 mole% of this material. On this basis, the yield of chlorides is ~44%. Pure samples of each chloride were obtained by preparative glc (same conditions as above) for spectral analysis.

trans-Di-(1-chlorovinyl)cyclopropane (XLIX) (11.8% relative yield): ir 3100, 3020, 1625, 993, 877, 700, 670 cm^{-1}; nmr τ 4.83 ABX quartet (4H), J = 5, 1 Hz, vinyl protons; 8.00 downfield portion of an A_2B_2 system further split to give an A_2B_2X pattern (2H),

J = 7.2, 1 Hz, cyclopropyl protons α to the vinyl groups; 8.83 upfield portion of an A_2B_2 system (2H), J = 7.2 Hz, cyclopropyl protons β to the vinyl groups.

trans-1,1-Dichloroethyl-1-chlorovinylcyclopropane (L) (47.8% relative yield): ir 3100, 3005, 2987, 2937, 2867, 1625, 993, 878, 705, 670 cm^{-1}; nmr τ 4.78 ABX quartet (2H), J = 6, 1 Hz, vinyl protons; 7.80 singlet (3H) methyl protons; 7.90-8.30 downfield portion of an ABCD system further split to an ABCDX pattern, cyclopropyl protons α to substituent groups; 8.80 upfield portion of an ABCD system, cyclopropyl protons β to substituent groups.

trans-Di-(1,1-dichloroethyl)cyclopropane (LI) (17.6% relative yield): ir 3005, 2987, 2937, 2867, 993, 707 cm^{-1}; nmr τ 7.78 singlet (6H) methyl protons; 8.05 downfield portion of an A_2B_2 system (2H), J = 7.3 Hz, cyclopropyl protons α to the chloroethyl groups; 8.80 upfield portion of an A_2B_2 system (2H), J = 7.3 Hz, cyclopropyl protons β to the chloroethyl groups.

For method of assignment of coupling constants, see below.

Reaction of XLVIII with Triphenylphosphine Dichloride

Triphenylphosphine dichloride was prepared in situ. Into a 125 ml 3-necked flask equipped with reflux condenser and gas inlet and charged with a solution of 4.14 g (0.0158 m) of triphenylphosphine in 70 ml of benzene was passed chlorine until it appeared no more oily precipitate formed. Diketone XLVIII (1 g, 0.0079 m) was added and the mixture warmed to 70°. The mixture was allowed to cool

and 1.6 g (0.016 m) of triethylamine was added slowly. The contents of the flask were again brought to 70° and maintained there for 3 hr. Nmr analysis of the mixture at this point showed absorptions due to the dione methyls and new absorptions at 4.4 (s), 7.2 (t), and 8.5 (t) τ. However glc analysis (column F at 105°) showed no peaks due to chlorides XLIX, L, or LI.

trans-1,2-Diethynylcyclopropane (XVIII)

To a 2000 ml 3-necked flask equipped with reflux condenser, mechanical stirrer, argon inlet and dropping funnel was added 1300 ml of t-butanol freshly distilled from sodium. After the system had been thoroughly flushed with argon, 67 g (1.72 m) of potassium was added in 5 g portions. After addition was complete, the mixture was brought to reflux. Within 2 hr most of the potassium had reacted, the remaining few milligrams were destroyed by addition of 2 ml of ethanol. The mixture still being at reflux, a solution of 48 g (~0.19 m) of chlorides XLIX, L, and LI in 70 ml of t-butanol was added dropwise over 0.5 hr. The progress of the reaction was monitored by glc (column F at 105°). During two hours the peaks due to the chlorides rapidly diminished as peaks at rt 1.0, 1.7, 2.2, and 2.7 min appeared and grew larger. The peak at 1.0 min is due to diacetylene XVIII-t and while the identities of the others are not known they are probably monoacetylenic intermediates. As the reaction progressed the intermediate peaks gradually diminished leaving mostly XVIII. At this point the dark brown reaction mixture

was allowed to come to room temperature and 300 ml portions were poured into 2000 ml of ice water. The cloudy aqueous solutions were extracted with 100 ml and 50 ml portions of pentane. The combined pentane extracts were filtered from polymeric material, washed with water and brine and dried over anhydrous sodium sulfate. The red-orange pentane solution, subjected to distillation at 20°/10-15 mm, yielded a clear distillate (A) and a dark red residue (B). Glc analysis (column F at 50°) of both A and B showed the presence of acetylene XVIII (rt 4.1 min). Residue B was distilled at 30°/12 mm to give 2.71 g of a slightly yellow liquid (C). Glc analysis of C showed it to be >90% trans-XVIII, the main impurities being due to longer retention time materials. Further distillation of residue B gave 3 g of a complex mixture containing <5% XVIII. Pentane was removed from distillate A by slow distillation through a 24" vacuum jacketed tantalum wire column until about 20 ml of solution were left in the boiling flask. When D was cooled to -78° a slightly yellow liquid (E) separated from the pentane weighing 1.41 g and consisting of 80-90% XVIII (the rest being mostly pentane). The distillation process was continued for the supernatant until 8 ml of solution remained which, after cooling to -78°, yielded 0.83 g of 80-90% pure XVIII (F). Samples E and F were combined to give G. The supernatant from F still contained a considerable quantity of XVIII. Recovery of this material by preparative glc (column G at 90°, rt 7 min) gave 0.45 g of pure trans-XVIII (H). The total yield from samples C, G and H is 5.40 g (~30%). Under the above conditions, no cis-XVIII was

detected. However if the reaction is run at 25° using diglyme as solvent and commercial potassium t-butoxide as base, the product consists of a 85/15 mixture of trans-XVIII and cis-XVIII, respectively. Also, under these conditions, the reaction is much faster although the yield is somewhat less (20%). Pure samples of trans and cis-XVIII were prepared by preparative glc (column G at 90°, rt cis-XVIII 9 min).

trans-XVIII: ir 3310, 3010, 2140, 1220, 1060, 920, 650 cm^{-1}; nmr (220 MHz) τ 8.28 singlet (2H) acetylenic protons; 8.47 triplet (2H), J = 7.0 Hz, propargyl protons; 8.92 triplet (2H), J = 7.0 Hz cyclopropyl protons; nmr (60 MHz) τ 8.20 doublet (2H), J = 1.5 Hz, acetylenic protons; 8.40-8.70 low field half of an A_2B_2 system (2H) propargyl protons; 8.80-9.1 high field half of an A_2B_2 pattern (2H) cyclopropyl protons; ms (70 ev) m/e (% base peak) 90 (16), 89 (100), 86 (4), 63 (52), 51 (32), 39 (38).

Analysis calc. for C_7H_6: C 93.34%, H 6.66%; found: C 92.82 %, H 6.72%.

cis-XVIII: ir 3310, 3010, 2130, 1220, 1040, 960, 650 cm^{-1}; nmr (220 MHz) τ 8.19 singlet (2H) acetylenic protons; 8.47 doublet of doublets (2H), J = 8.5, 7.0 Hz, propargyl protons; 8.88 six line pattern, (1H), J = 8.5, 4.5 Hz, cyclopropyl proton trans to the ethynyl groups; 9.09 six line pattern (1H), J = 7.0, 4.5 Hz, cyclopropyl proton cis to the ethynyl groups; ms (70 ev) m/e (% base peak) 90 (14), 89 (100), 86 (3), 63 (49), 51 (24), 39 (27).

Reaction of chlorides XLIX, L, and LI with bases other than potassium t-butoxide did not improve the yield of XVIII. These experiments are summarized below:

1. Reaction with sodium dimsylate. A solution of sodium dimsylate (0.01 m) in DMSO was prepared by the method of Corey and Chaykovsky (130). To this cloudy solution at 25° was added a solution of 1 g of the chloride mixture in 4 ml of DMSO. The system was connected to a water aspirator through a reflux condenser, dry ice trap and drying tube. The pressure of the system was reduced to 25 mm and the mixture heated to 80°. After 30 min ~50 μl of liquid had collected in the trap. Analysis of this liquid by glc showed no XVIII to be present.

2. Reaction with potassium hydroxide. The apparatus was similar to that used in 1. To a mixture of 3 g of powdered KOH and 15 ml of a 60/40 mixture of glycol and tetraglyme at 140-150° was added 0.5 g of the chlorides. After stirring for 0.5 hr at this temperature, 75 μl of distillate were collected. Glc analysis revealed at least 15 peaks in addition to a small peak due to XVIII. A similar experiment in hexamethylphosphoramide gave ~1% of XVIII.

3. Reaction with sodium octanoxide. The reaction of sodium octanoxide (prepared by heating a mixture of 0.8 g of sodium and 20 ml of octanol at 110° until the sodium had disappeared) with 0.5 g of chlorides at 140°/25 mm yielded 100 μl of distillate of which XVIII constituted less than 5%.

4. Reaction with sodamide. The reaction of 0.060 g of sodamide in 3 ml of mineral with 0.10 g of the chlorides at 135°/25 mm for 1 hr gave only a small amount of recovered starting chlorides. The reaction of sodamide in liquid ammonia with chlorides gave no XVIII (131). Reaction in decane at 125° gave only starting material.

5. Reaction with potassium 3-methyl-3-pentoxide. The base was prepared by the reaction of potassium with 3-methyl-3-pentanol at 120° and was stored as its pentane solution. Reaction of 0.98 g of the base with 0.20 g of the chlorides in 10 ml of pentane gave after 36 hr at 25° XVIII in ~15% yield.

6. Reaction with sodium methoxide. The reaction of 0.14 g of sodium methoxide and 0.10 g of the chlorides in 3 ml of diglyme at 100° for 2 hr gave XVIII in 10-20% yield.

7. Reaction with lithium diethylamide. To a solution of 0.0002 m of lithium diethylamide (prepared from reaction of n-buLi with diethylamine) was added 0.010 g of chlorides. Glc analysis showed less that 5% of XVIII.

8. Reaction with diazabicyclononene (DBN). A mixture of 1.24 g of DBN, 0.5 g of the chlorides and 10 ml of triethylene glycol was heated for 3 hr at 100° under argon. After treatment with water and pentane 0.1 g of a liquid was isolated. Glc and nmr analysis showed this liquid to consist of 90% XLIX and 5% L.

Equilibration of cis- and trans-XVIII

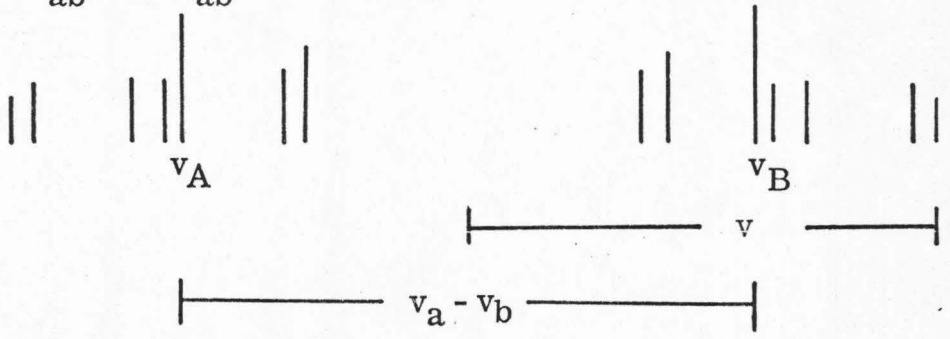
To a single-necked 5 ml flask equipped with a magnetic spinbar and a rubber serum cap was added 1 ml of dry DMSO and 0.15 g of potassium t-butoxide. The system was flushed with argon and 0.01 g of trans-XVIII was added via a 50 μl syringe. Aliquots taken at 5 and 30 min were added to water and the organic products extracted with pentane. Glc analysis (column H at 45°) of both aliquots showed trans- and cis-XVIII to be present in 74/26 ratio. The yield of this reaction appears to be poor, a substantial amount of black polymer having formed. Equilibration attempts using sodium methoxide or lithium diethylamide failed.

Analysis of Splitting Patterns

The four spin systems of trans substituted cyclopropanes may be of the type AA'BB' or AA'XX' depending on the relative chemical shifts of the proton groups. AA'XX' systems are characterized by the symmetry properties of the two groups of absorptions. The A and the X groups are mirror images of each other and each is a symmetrical multiplet. The pair of apparent triplets observed in the spectra of trans-XVIII at 220 MHz and diketone XLVIII constitute the simplest type of AA'XX' splitting pattern. Reference to theoretical line spectra given in the appendix of reference 131 shows that triplets occur for AA'XX' systems when $J_{AX} = J_{AX'}$. Such a case is referred to as A_2X_2. The cis or trans coupling constant may be calculated from the relationship derived for A_2X_2 systems: $N/2 = J_{AX}$

where N equals the chemical shift difference between the first and last lines of the triplet. For trans-XVIII, N = 14 and J_{AX} = 7 Hz. The same values are obtained for diketone XLVIII.

The ring proton absorption patterns for dichloride XLIX, tetrachloride LI and trans-XVIII at 60 MHz are more complex (Figures 7, 8, and 6a). The two groups are still mirror images of each other but are not symmetric themselves. (The downfield group of trans-XVIII is further split by interaction with the acetylenic proton so just the upfield group will be analyzed.) These symmetry properties are characteristic of AA'BB' spectra. The 16 line patterns may be compared to theoretical line spectra and again the observed patterns most closely fit those patterns for which $J_{ab} = J_{ab'}$. Because A_2B_2 spectra are second order all the coupling constants cannot be reported without the aid of a computer program designed to reproduce spectra. However it is possible to calculate the cis or trans coupling constant using the relationship $v = \frac{1}{2}N + \frac{1}{2}[(v_a - v_b)^2 + N^2]^{\frac{1}{2}}$ where v equals the chemical shift of the last line of the A or B group relative to the midpoint between the groups, $v_a - v_b$ equals the separation between the groups, and N equals 2 J_{ab} or 2 $J_{ab'}$. These relationships are illustrated below.



Results of these calculations are summarized in Table XVIII. The same coupling constants for trans-XVIII are derived from either the 220 or 60 MHz spectra. This is an important back check on the equations used. The fact that all the compounds listed have very nearly equal coupling constants implies that the sum of the effects due to the electronegativity of the substituent groups is about equal. There have been several reports which show a linear relationship between electronegativity of the substituent groups and coupling constants of the ring protons for cyclopropanes (133).

Table XVIII. Coupling Constants of Cyclopropanes

Compound[a]	Pattern	v	$\nu_a - \nu_b$	J_{cis}	J_{trans}	J_{gem}
trans-XVIII[b]	A_2X_2		100	7.0	7.0	
trans-XVIII	A_2B_2	24	29	7.1	7.1	
cis-XVIII[b]	A_2MX			7.0	8.0	-4.5[c]
diketone-XLVIII	A_2X_2		64	7.0	7.0	
tetra-LI	A_2B_2	31	45	7.3	7.3	
dichl-XLIX	A_2B_2	33	49	7.2	7.2	
tri-L	ABCD					

[a] Taken at 60 MHz unless otherwise noted.

[b] Taken at 220 MHz.

[c] Assumed to be negative.

[d] Given in Hertz.

The 220 MHz spectrum of cis-XVIII was analyzed by first order methods. The 60 MHz spectrum of this compound should display an A_2BC pattern but unfortunately it was too poorly resolved for analysis. The coupling constants obtained from the 220 MHz spectrum are listed in Table XVIII. The splitting pattern for trichloro L is ABCD, and was too complicated for even simple analysis as in the A_2B_2 cases.

Pyrolysis of trans-XVIII. Preparation of Bicyclo[3.2.0]hepta-1,4,6-triene (I), Fulvenallene (LV), Ethynylcyclopentadiene (LVI), and Heptafulvalene (LVII)

Application of the atmospheric flow system described in the preparation of LIV to the pyrolysis of XVIII gave a 30-40% yield of I. For most of the preparations of I however the vacuum flow system was employed. A schematic of this system is given in Figure 23. The section of tubing through the oven is made of quartz.

A 25 ml single-necked pear shaped flask containing 0.10 g of trans-XVIII and 2 ml of hexane was attached to the system at point A. The mixture was frozen in liquid nitrogen and evacuated through the degass line, stopcocks C and E being closed. After the evacuation was complete (0.02 torr) stopcock B was closed and the mixture warmed to room temperature. After melting was complete and gas evolution had ceased, the solution was frozen and stopcock B reopened. After degassing to 0.02 torr stopcocks B and F were closed and stopcock C opened. The liquid nitrogen bath was removed from A

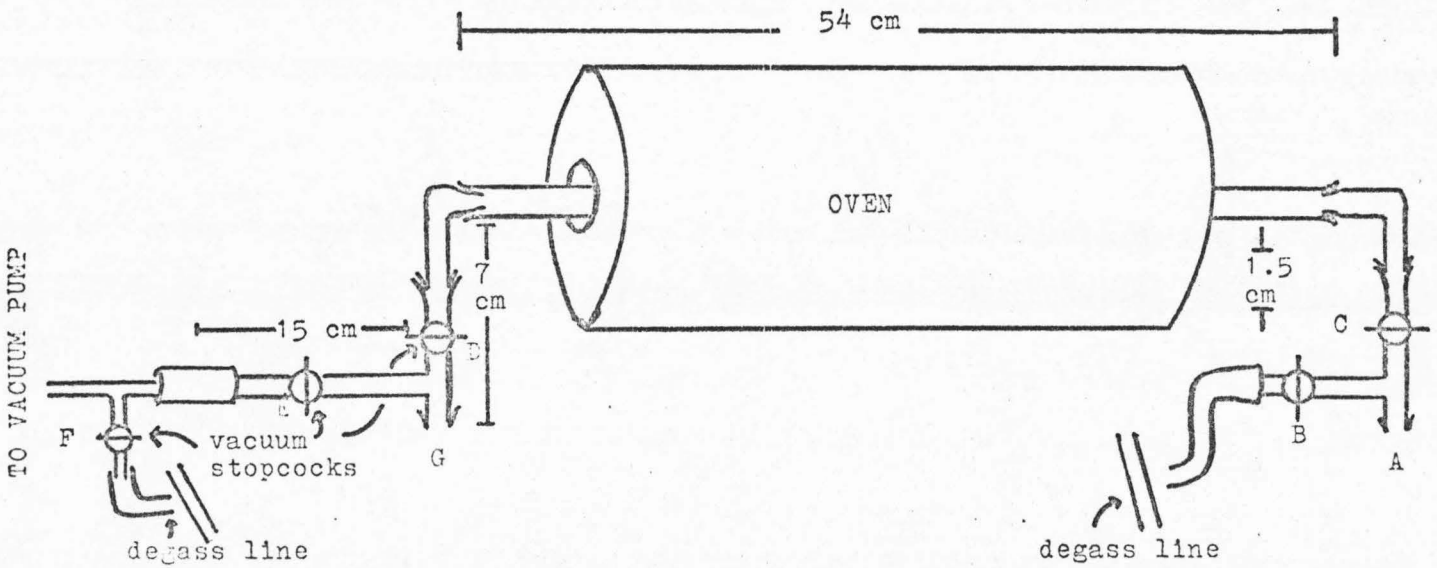


Figure 23. Vacuum Flow Pyrolysis Unit

and placed under the collection flask at G. The contents of the flask at A were warmed to room temperature with a water bath and allowed to vaporize through the heated quartz tube (485°) and condense in the flask at G. The same procedure was repeated for two more passes through the heated tube. Reaction was usually complete at this point. The flask containing the yellow condensate was removed from the system and stored in dry ice. Upon analysis by glc (column F at 50°) the pyrolysis mixture showed the presence of triene I (rt 105 min), fulvenallene (LV, rt 8.5 min) and ethynylcyclopentadiene (LVI 6.7 min) in 80:15:5 ratio. Each product was isolated by preparative glc (column F at 90°) to give the following spectral data:

Bicyclo[3.2.0]hepta-1,4,6-triene. (I, rt 16.5 min), ir 3100, 3075, 3885, 2810, 2340, 1645, 1415, 1305, 1270, 1180, 1055, 945, 935, and 885 cm^{-1}; nmr τ 3.27 five line pattern (2H), J = 1, 1 Hz, cyclobutenyl protons; 4.92 seven line pattern (2H), J = 2, 1 Hz, cyclopentadienyl vinyl protons; 6.62 seven line pattern (2H), J = 2, 1 Hz, cyclopentadienyl aliphatic protons (see Figure 24); uv (cyclohexane) λ_{max} 204 (log ϵ = 4.0), 272 (log ϵ = 3.0) nm. (extinction coefficients are approximate); ms (70 ev) (% base peak), 90 (65), 89 (100), 86 (4), 63 (66), 51 (18), 39 (28).

Fulvenallene (LV, rt 13.8 min), ir 3115, 3078, 1970, 1950, 1918, 1690, 1625, 1480, 1425, 1380, 1320, 1260, 1165, 1075, 885, 850 cm^{-1}; nmr τ 3.65 multiplet (4H) ring protons; 4.70 multiplet (4H) allenyl protons; uv (cyclohexane) λ_{max} 250 (log ϵ = 4.0),

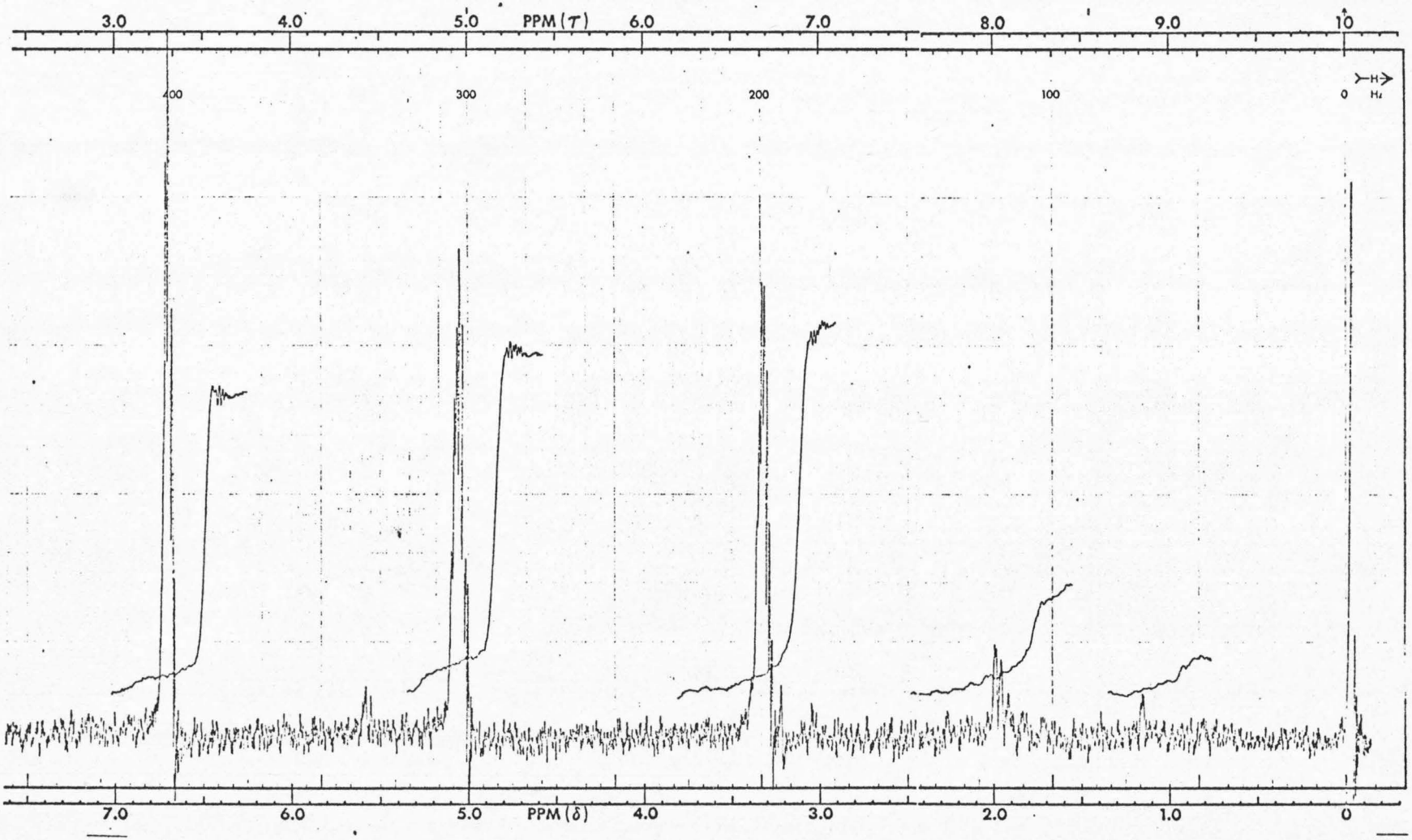


Figure 24. 60 MHz Nmr Spectrum of Bicyclo[3.2.0]hepta-1, 4, 6-triene in CCl_4

340 (log ϵ = 2.5) nm (extinction coefficients are approximate); ms (70 ev) (% base peak) 90 (100), 89 (100), 86 (5), 63 (66), 51 (18), 39 (28).

Ethynylcyclopentadiene (LVI, rt 12.3 min) ir 3310, 3100, 2900, 2105, 1600, 1372, 1355, 1280, 1185, 1160, 1005, 958, 898, 680, 645; ms (70 ev) (% base peak) 90 (100), 89 (95), 86 (4), 63 (58), 51 (13), 39 (31). Absolute yield of I, LV, and LVI is 70-80%. A black, pentane soluble material was left in flask G after the first pass. This material is heptafulvalene and constitutes <1% of the total reaction products: ir 3100, 2980, 1560, 1260, 1100, 1010, 712 cm^{-1}; nmr 4.20 τ broad multiplet.

Bicyclo[3.2.0]hepta-2,6-diene (134)

A solution of 0.5 ml of freshly distilled cycloheptatriene in 60 ml of ether was subjected to direct irradiation from a Hanovia medium pressure lamp. The reaction, followed by glc (column H at 45°, rt triene 12.0 min, rt diene 7.4 min) reached 75% conversion after 10 hours. The slightly yellow solution was concentrated by vacuum transfer of the ether at -20° to -40°/1 mm. Separation was only moderately efficient but from the concentrated solution obtained it was possible to isolate 0.060 g of bicyclo[3.2.0]hepta-2,6-diene. The nmr of this compound corresponds to that reported by Dauben and Cargill (133).

Bicyclo[3.2.0]heptane (134)

Bicyclo[3.2.0]hepta-2,6-diene was hydrogenated at atmospheric pressure. After about 5 mg of platinum oxide had been prereduced in 7 ml of ethanol and 0.059 g of the diene in 2 ml of ethanol had been added, hydrogen uptake was monitored. After 29 ml (98%) of hydrogen had been absorbed uptake ceased. The ethanol solution was filtered from platinum and added to water. The aqueous mixture was extracted with 1 ml of pentane, the pentane layer washed with water and dried over anhydrous magnesium sulfate. Glc analysis (column H at 45°, rt 5.7 min) showed the reaction to be complete. Bicyclo[3.2.0]heptane was isolated by preparative glc (column G at 80°): ir 2945, 2865, 1470, 1445, 1320, 1305, 1285, 1250, 1220, 1170, 1130, 940, 885 cm^{-1}.

Hydrogenation of I

Triene I resulting from the pyrolysis of 0.070 g of trans-XVIII in 1 ml of hexane at 485/0.02 mm was isolated by preparative glc (column G at 90°) and reduced in the manner above. Absorbed was 25 ml of hydrogen corresponding to 0.025 g of triene I. Treatment of the reaction mixture as above and subsequent glc analysis (column H at 45°) showed the reaction to be complete and the presence of two new peaks at rt 4.3 and 5.7 min in a 15/85 ratio. The peak at 5.7 min corresponds to bicyclo[3.2.0]heptane while the identity of the other peak is unknown. The bicycloheptane was isolated by preparative glc and its ir spectrum was superimposable upon that

obtained above.

6-Chlorofulvene

A 50 ml 3-necked flask equipped with a magnetic spinbar, reflux condenser nitrogen inlet and dropping funnel was charged with 1 g (0.0152 m) of cyclopentadiene (freshly prepared from its dimer), 3.35 g (0.0298 m) of potassium t-butoxide and 15 ml of pentane. The system was flushed with nitrogen and the temperature of the cooling bath lowered to -20° to -30°. Chloroform (3.6 g, 0.033 m) was added dropwise over 30 min and the resultant dark brown mixture allowed to stir for an additional 10 min at -20°. The mixture was added to ice water, the pentane layer separated and the aqueous layer extracted once with 10 ml of pentane. The combined pentane layers were washed with water and brine and dried over anhydrous sodium sulfate. Distillation of pentane at 10°/50 mm gave a red-brown foul smelling oil. Further distillation of this oil at 25°/0.02 mm gave 0.17 g of an orange liquid. Glc analysis (column I at 60°) showed the presence of three products at 14, 17, and 22 min retention time in a ratio of 22:8:70. The peak at 14 min is due to 1,1-dichloro-2,2-dimethylcyclopropane; nmr τ 8.63 singlet (3H); 8.82 singlet (1H). The peak at 17 min is assigned to chlorobenzene on the basis of spiking experiments and from the presence of a broad singlet at 2.74 τ in the nmr of the reaction mixture. The remaining peak is due to 6-chlorofulvene. This assignment is made on the basis of spectral and chemical evidence (see below): ir 3080, 1660, 1610,

1620, 1480, 1365, 1325, 1275, 1090, 830 cm^{-1}; nmr τ 3.22 broad singlet (1H) exomethylene protons; 3.42-3.70 multiplet (3H), ring protons; 3.82-4.0 multiplet (1H) ring proton; uv (cyclohexane) λ_{max} 261 (log ϵ = 4.43), 268 (log ϵ = 4.42), 277 (log ϵ = 4.18), 371 (log ϵ = 2.53) nm. 6-Chlorofulvene is an orange, air sensitive oil; its yield in this reaction is 10%.

6-Piperidinylfulvene

To a 10 ml flask containing 1 ml of piperidine at 25° was added dropwise ~0.10 g of the reaction mixture above. The reaction is quite exothermic, a hissing sound being made after the addition of each drop of the mixture. After stirring for 30 min under nitrogen, the orange mixture was added to 7 ml of pentane. The resultant floculent precipitate, separated from pentane by centrifugation and washing, was dried to give 20 mg of piperidinyl hydrochloride mp 245-247°. The yellow supernatant was distilled at 25°/60 mm to remove pentane and finally at 25°/0.02 mm to remove piperidine. The dark brown residue was dissolved in cyclohexane and boiled for 1 min with 5 mg of activated charcoal. After filtration through a fritted glass funnel, the cyclohexane was distilled off leaving a dark yellow semi-solid. A portion was crystallized from pentane to give 6-piperidinylfulvene as yellow leaflets mp 66-67° (lit. (47) 67°): ir 3100, 3080, 2955, 1620, 1405, 1360, 1220, 1125, 1080, 910, 730 cm^{-1}; nmr τ 3.29 singlet (1H); 3.71 triplet (2H), J = 2 Hz; 3.95 triplet (2H), J = 2 Hz; 6.50 multiplet (4H); 8.32 broad singlet (6H);

uv (cyclohexane) λ_{max} 323 (log ϵ = 4.36) nm (lit. (47) 322 (log ϵ = 4.50) nm).

Reaction of Chloroform with Sodium Cyclopentadienide

To a 3-necked 100 ml flask equipped with magnetic spinbar, reflux condenser, argon inlet and dropping funnel was added 2.56 g of 57% sodium hydride dispersion (0.061 m). Mineral oil was removed from the dispersion by repeated washes with pentane. To the sodium hydride was added 30 ml of dry THF and the mixture brought to 0°. Cyclopentadiene (4.0 g, 0.061 m) was added in portions and the mixture allowed to stir for 15 min at 20° under argon. After reducing the temperature to -20° chloroform (3.6 g, 0.033 m) was added dropwise over 40 min. After stirring an additional 15 min, the mixture was added to ice water and extracted with pentane. The yellow pentane solution was washed with water, dried over anhydrous sodium sulfate and concentrated. Glc analysis of the concentrate showed neither chlorofulvene nor chlorobenzene to be present.

Reaction of I with Potassium t-Butoxide

Into an nmr tube flushed with argon was syringed a solution of triene I (prepared from 0.10 g of trans-XVIII) in 0.7 ml of dry DMSO-d_6. An nmr spectrum of this solution displayed the usual triene absorptions. To this solution was added about 50 μl of a solution of 0.10 g of potassium t-butoxide in 0.5 ml of DMSO-d_6. Immediately the solution turned brown; the areas of the nmr

absorptions of I were still in 1:1:1 ratio. No change in the ratio was observed after 10 min. About 100 μl more of the base solution was added; all resonances decreased in intensity but the ratio of the peak areas remained at unity. A third addition of base virtually destroyed all of triene I. An nmr of the resultant black, turbid mixture displayed peaks at 3.60-4.45 τ (multiplet) and at 6.80 τ (multiplet). These peaks are of weak intensity but compare very well in shape and position to a spectrum of the undeuterated dimers III and IV supplied by Professor P. R. Radlick except that the resonances at 6.3 τ corresponding to the bridgehead protons were missing. This suggests that the dimers are dideuterated in the bridgehead position. Glc analysis (column E at 150°) of the pentane extract of the reaction mixture showed the presence of peaks of equal area at 28 and 30 min. The yield of dimers is estimated to be 5%.

Reaction of I with Alkali Metals

1. To a mixture of 0.025 g of potassium and 0.3 ml of dry THF under argon in the bulb of apparatus I depicted in Figure 26 was added about 0.03 g of I in 0.20 ml of dry THF. After stirring for 1.5 hr at 25°, the potassium had turned black and the solution brown-red. The mixture was filtered into the nmr tube and subsequent nmr analysis showed the presence of a 1:1 mixture of dimers III and IV and triene I: nmr (dimers) τ 3.75-4.3 multiplet, vinyl protons; the upfield protons were obscured by the peaks due to THF. Methanol was added and the mixture allowed to evaporate. Pentane was added

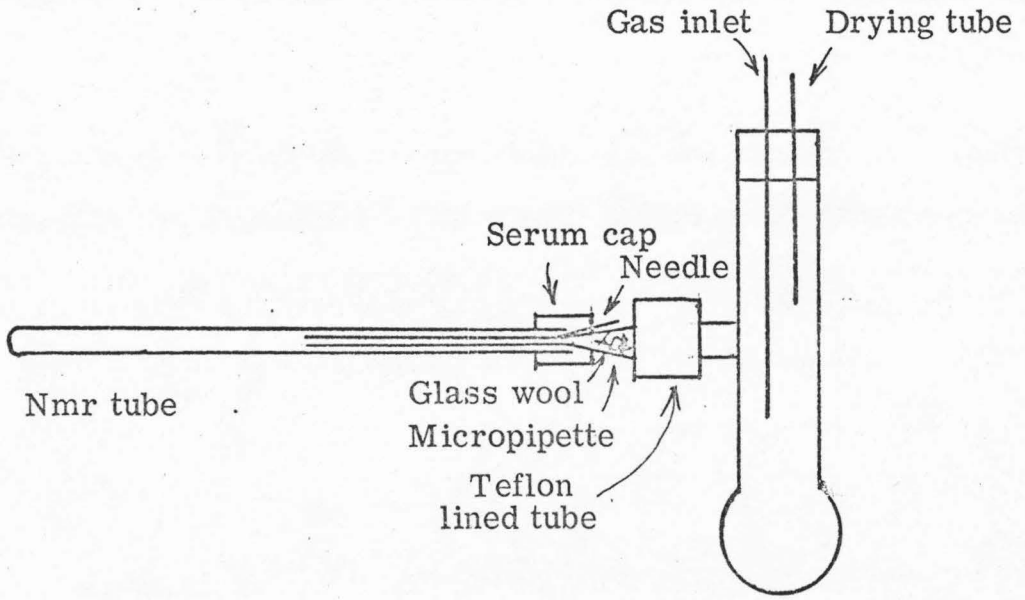


Figure 26. Apparatus I for Anion Experiments

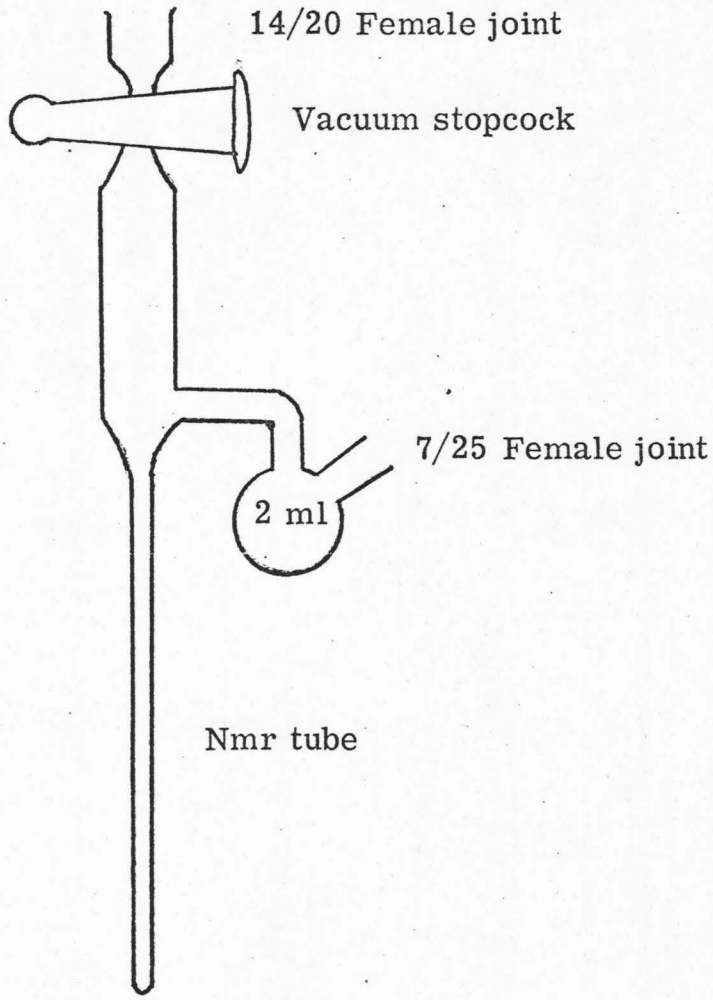


Figure 27. Apparatus II for Anion Experiments

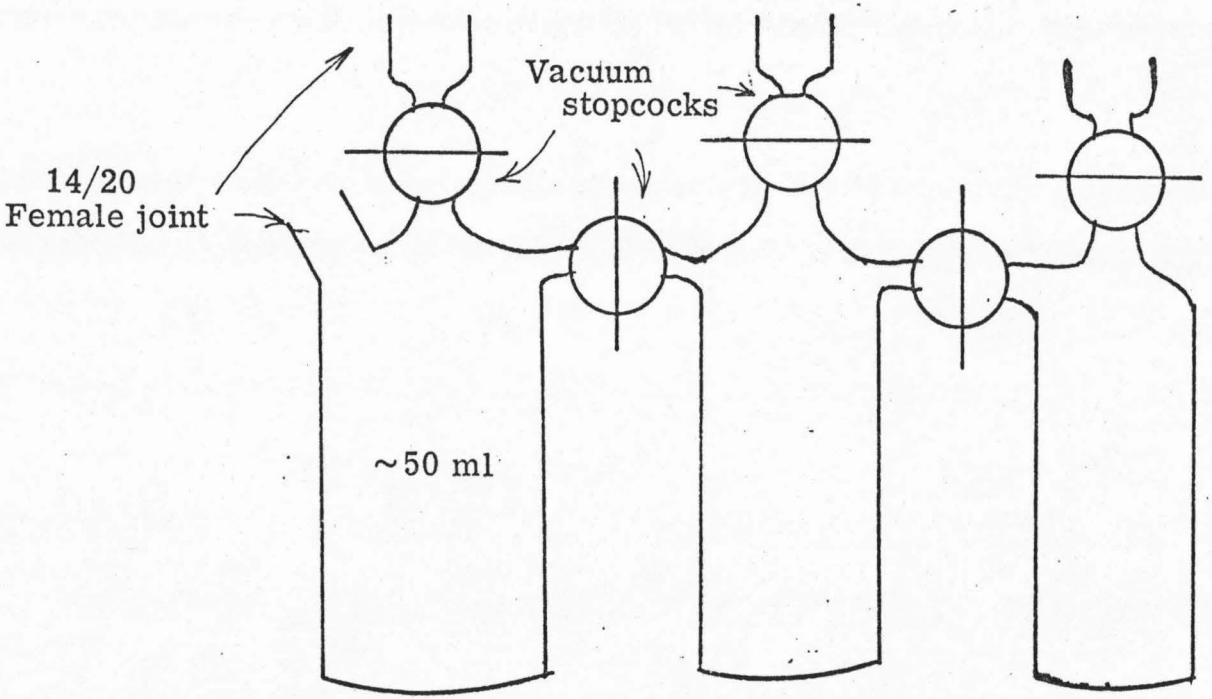


Figure 28. Apparatus III for Anion Experiments

to the polymeric residue and glc analysis (column F at 120°) confirmed the presence of dimers (rt 7.9, 8.5 min).

2. To the bulb of apparatus II (Figure 27) was added 0.015 g of potassium. The bulb was stoppered and the pressure in the system reduced to 5×10^{-4} torr. After 10 min about 0.03 g of triene I and then 0.4 ml of a mixture of THF and tetramethylsilane which had been stored over potassium were vacuum transferred into the nmr tube. Keeping the THF-I mixture frozen in liquid nitrogen, the potassium was distilled with a small flame out of the bulb and into the side arm where it formed a mirror. The bulb was sealed off from the rest of the system. The stopcock was closed and the THF-I mixture allowed to melt and run over the potassium mirror. Immediately bubbling was evident and the solution turned light brown. Apparently reaction stopped quickly because of the formation of a brown polymeric coating on the potassium. The solution was allowed to run back into the nmr tube, was frozen and the tube sealed at 10^{-4} torr. Nmr analysis of the solution showed it to consist of a mixture of dimers III and IV and triene I in a 4/1 ratio. The presence of dimers was confirmed by glc.

3. To the bulb in apparatus II was added 30 μl of 1:4 sodium potassium alloy, a magnetic spinbar, and a small amount of xylene. The bulb was stoppered and the system evacuated to 10^{-4} torr to remove xylene and to establish a high vacuum for the rest of the experiment. About 0.3 ml of THF was vacuum transferred from lithium aluminum hydride into a flask containing calcium hydride. About 0.02 g of I was transferred into the same flask. After five

min the THF-I mixture was vacuum transferred into the bulb containing the alloy, the stopcock closed and the whole mixture allowed to come to room temperature with stirring. After 5 min the solution had turned yellow brown and was decanted into the nmr tube, frozen and the tube sealed at 10^{-4} torr. Nmr and glc analysis showed only dimers to be present.

Reactions with Naphthalene Radical Anion

1. Cyclopentadiene. To 7 ml of dry THF in a 25 ml 3-necked flask equipped with glass coated magnetic spinbar and serum cap was added 0.14 g (0.006 m) of sodium and 0.78 g (0.006 m) of naphthalene as the system was flushed with argon. After a few min a green color developed and rapidly darkened. After stirring for one hr cyclopentadiene was added dropwise and after ~0.30 g had been added the reaction mixture turned colorless. It was noted that not all of the sodium had reacted with the naphthalene prior to the addition of cyclopentadiene. About one ml of this clear solution was added to water and the resultant cloudy white oil dissolved in pentane. After drying, the pentane was removed by distillation at 20°/50 mm leaving a white solid: nmr τ 2.2-2.8 A_2B_2 relative area 3; 3.0, 4.2, and 6.7 τ relative area 2. The first set of absorptions is due to naphthalene and the second set to 1,4-dihydronaphthalene. Considering that the naphthalene had only partially reacted it appears that naphthalene and 1,4-dihydronaphthalene had formed in equal amounts after addition of cyclopentadiene.

2. 1, 4-Pentadiene. In a similar fashion to above a solution of the radical anion was prepared from 0.05 g (0.0022 m) of sodium, 0.28 g (0.0022 m) of naphthalene and 5 ml of dry THF. After two hr the sodium had completely reacted. To this solution was added 0.149 g (0.0022 m) of 1, 4-pentadiene (freshly distilled from lithium aluminum hydride). After addition was complete, the mixture remained dark green but slowly turned brown and then red over the next two hours. At this point D_2O was added whereupon the solution turned colorless. The clear solution was added to pentane-water, and the pentane layer was separated and dried over anhydrous sodium sulfate. Removal of the pentane by distillation left a white residue. Nmr analysis of the residue showed the presence of ~5% 1, 4-dihydronaphthalene and ~95% naphthalene.

3. Cycloheptatriene. A solution of the radical anion was prepared from 0.08 g (0.0035m) of sodium, 0.45 g (0.0035 m) of naphthalene and 5 ml of dry THF. To this solution was added 0.322 g (0.0035 m) of cycloheptatriene. The color of the mixture immediately changed from dark green to a very intense blue. Nmr analysis of an aliquot of this blue solution showed the presence of only very poorly resolved absorptions due to solvent and naphthalene. The blue solution was quenched with D_2O to give an orange cloudy mixture. Nmr analysis of this mixture showed the presence of naphthalene and a very small amount of 1, 4-dihydronaphthalene (1%). No absorptions due to cycloheptatriene were present.

4. Triene I. A solution of the radical anion was prepared from 0.072 g (0.0056 m) of naphthalene, 0.013 g (0.00056 m) of sodium and 1 ml of dry THF in chamber A of apparatus III (Figure 28). After the radical anion solution had been stirring for two hours, 0.05 g (0.00055 m) of triene I was vacuum transferred into chamber B. The solution in A was degassed by two freeze-thaw cycles; both A and B were then free of any residual oxygen. The contents of B were vacuum transferred into A by cooling A to -78° and opening stopcock 1. After transfer was complete, the contents of A were allowed to warm to room temperature. After stirring for 5 min, the vacuum was broken with argon and D_2O added to the green brown mixture. The resultant orange mixture was extracted with pentane. Nmr analysis of the residue left after removal of pentane showed only the presence of deuterated dihydronaphthalene and naphthalene in 1:5 ratio. None of dimers III and IV were detected but about 0.03 g (80%) of polymer was isolated from the pentane layer.

Reaction of I with Amide Bases

1. 1,4-Pentadiene and potassium amide. Into the bulb of apparatus II was condensed 1.5 ml of anhydrous ammonia at -78°. A small piece of potassium was added whereupon a deep blue coloration developed. Addition of a small crystal of $Fe(NO_3)_3 \cdot 9\,H_2O$ caused decolorization upon warming to -40°. Pieces of potassium were added slowly until a total of 0.075 g had been added. The dark grey mixture was allowed to stir for 5 min and 0.10 g of 1,4-pentadiene in

0.1 ml of hexane was added dropwise at -78°. After the first drop the mixture turned deep yellow and remained this color as the rest of the diene was added. Upon warming the yellow mixture to -40° it turned deep red but turned yellow again upon cooling to -78°. About 1 ml of the mixture was filtered into the nmr tube by first cooling the flask up to the side arm to -40 and then tilting the flask so that the nmr tube was buried in a Dewar flask containing dry ice. The flask was tilted slowly so that the liquid ammonia solution flowed into the nmr tube through the glass wool filter. Nmr analysis of the contents of the tube is given in Table VII. The mixture gave the same spectrum at -70° or -40°.

2. Triene I and potassium amide. In a manner exactly the same as above, an nmr sample was prepared of a mixture of 0.75 ml liquid ammonia, 0.05 g of potassium and 0.05 g of triene I. Nmr analysis of the brownish solution at -70° showed no absorptions other than that due to ammonia. At -50° the mixture was subjected to the computer average of transients technique (CAT) for 10 scans. However no new absorptions were found. Upon ethanol workup of the ammonia solution only polymer was isolated. No dimers were detected.

3. Triene I and lithium bis-trimethylsilylamide (66). Into a heat dried 5 ml single-necked flask equipped with a magnetic stirrer was added 0.4 ml of hexane and 0.036 g of bis-trimethylsilylamine (hexamethyldisilazane). The flask was stoppered with a serum cap

and flushed with argon. To this mixture was added 100 μl of a 2.23 M solution of n-butyllithium in hexane. After stirring for 5 min most of the hexane was blown off with argon. The flask was attached to a vacuum line and the remainder of the hexane distilled off leaving a colorless glassy solid. A mixture of 10 mg of triene I and 0.4 ml of dry THF was vacuum transferred onto the solid at -78°. After coming to room temperature and stirring for 5 min the contents of the flask were cooled to -78° and D_2O transferred in. Nmr analysis of the resultant mixture showed only unreacted triene absorptions and a broad hump at 3.6 τ. Addition of the mixture to water caused separation of a yellow musky solid which was insoluble in pentane. Extraction of the THF/water mixture with pentane followed by glc analysis showed no e III or IV to be present.

4. Triene I and lithium dicyclohexylamide. Dicyclohexylamine was distilled immediately before use, bp 93°/20 mm. Tetramethylenediamine was distilled from sodium, bp 120°, and stored over molecular sieves. To a mixture of 0.51 g (0.0044 m) of tetramethylethylenediamine, 0.54 ml of 2.03 M n-butyllithium (0.0011 m) and 10 ml of dry THF in chamber A of apparatus III was added 0.206 g (0.0011 m) of dicyclohexylamine. Into flask B was transferred a mixture of 0.05 g (0.00055 m) of I and 2 ml of dry THF. The solution in A was degassed with two freeze-thaw cycles. The mixture in B was slowly vacuum transferred into A over 3 hr by opening and closing stopcock 1. The contents of A were held at -78°

throughout the transfer. During the course of the addition the contents of A turned yellow and deposited a fine yellow precipitate. After the transfer was complete the mixture was stirred for 0.5 hr at -78°. The vacuum was broken with argon and the mixture quenched with 0.10 ml of methanol -O-d (99% Stohler). A mixture of 20 ml of water and 2 ml of pentane was added and the mixture stirred vigorously under argon. The organic layer was separated and subjected to distillation at 25°/0.001 mm to give residue A and distillate B. Residue A was dissolved in pentane, washed with dilute acetic acid and water and dried over anhydrous magnesium sulfate. Glc analysis of this solution showed the presence of dimers III and IV. Glc analysis of distillate B showed the presence of triene I. The total yield of dimers and triene is estimated to be ~5%. The different fractions were combined and subjected to glc-ms analysis. Analysis of the peaks due to III and IV gave parent peaks at m/e 182 corresponding to the incorporation of two deuteria per dimer molecule. Mass spectral analysis of the peak due to I showed the presence of an abnormally large peak at m/e 91 (30% of the m/e 89 peak as opposed to 5% of the m/e 89 peak for authentic I). It is not possible to determine exactly the amount of deuteration in recovered I lacking a mass spectrum of authentic monodeutero-I or a high resolution mass spectrum of recovered I. It was estimated that recovered I is 25% deuterated. However isolation of I by preparative glc followed by ir analysis showed no absorptions in the area expected for C-D stretch at the methylene position (~2000 cm^{-1}); also peaks not due to

I were discernible.

Reaction of I with Alkyllithiums

1. 1,4-Pentadiene and n-butyllithium (run A). A solution of 0.10 g (0.00146 m) of 1,4-pentadiene in 0.4 ml of THF was added to an nmr tube. The tube was flushed with argon and 0.83 ml of 2.0 M n-butyllithium in hexane (0.0016 m) was added at -78°. The mixture was allowed to warm to room temperature; at -10° an exothermic reaction took place, and the mixture separated into two layers. The top layer was discarded and nmr analysis performed on the bottom layer. The nmr spectrum obtained reproduced that reported by Bates et al. (59) for pentadienyl anion.

2. Triene I and n-butyllithium (run B). To 0.5 ml of 2.2 M n-butyllithium under argon in a 5 ml flask was added a solution of 30 mg of triene I in 0.2 ml of dry THF. The mixture was allowed to warm to room temperature during which time it changed in color from yellow to dark red. Nmr analysis of this solution showed new peaks at 4.68, 3.20 and 2.95 τ. However it was ascertained by a control experiment that these peaks were due to the mixture of n-butyllithium and THF. No peaks due to triene I or dimers III and IV were present. A repeat of this experiment at 25° (run C) gave the same results. In a third experiment (run E) none of III or IV were detected after addition of D_2O. A fourth experiment (run F) performed in vacuo resulted in observation of only broad humps at 3.6 and 5.0 τ upon nmr analysis. After quenching with methanol no dimers were

detected by glc. An experiment (run G) similar to C but using pentane as solvent gave after quenching only polymer. No dimers were present.

3. Triene I and n-butyllithium. Variable temperature nmr (run D). To the bulb in apparatus I (Figure 26) was added 0.6 ml of a 2.2 M n-butyllithim in hexane. The hexane was removed by an argon stream and after cooling the residue to -10° 0.5 ml of dry THF was added. The resultant solution was cooled to -78° under argon and a solution of 50 mg of triene I in 0.1 ml of THF/hexane was added dropwise. The yellow turbid mixture was decanted into the nmr tube and nmr spectra recorded at various temperatures. At temperatures -70°, -50°, -30°, -10°, and 0° no new peaks and no absorptions due to I were observed.

4. Triene and n-butyllithium and tetramethylethylenediamine (run H). Into a 5 ml flask on a vacuum line containing 90 μl of 2.03 M n-butyllithium was vacuum transferred 0.6 ml of tetramethylethylenediamine. This mixture was allowed to stir for 5 min in vacuo at 25° and then cooled to liquid nitrogen temperature. A mixture of 30 mg of triene I and 0.2 ml of tetramethylethylenediamine was vacuum transferred to the frozen solution. The resultant mixture was warmed to -40° and stirred for 15 min. D_2O was distilled into the reaction flask resulting in deposition of a white solid. Nmr analysis of the supernatant showed none of III or IV to be present. The white solid, being insoluble in ether or acetone, is probably polymer.

5. Triene and triphenylmethyllithium (run I). The normal glass stopper for apparatus II (Figure 27) was replaced with one which served also as a solid addition tube, having a right angle bend in the tube above the joint. Into the bend of this tube was placed 0.059 g of triphenylmethane. To the bulb was added 97 μl of 2.03 M n-butyllithium as the system was flushed with argon. The system was evacuated to 10^{-3} torr and 0.5 ml of dry THF was transferred into the bulb. Triphenylmethane was added to the THF-butyllithium mixture via the addition tube. The resultant deep red solution was allowed to stir for 5 min and was frozen at -196°. A mixture of 20 mg of triene I and 0.3 ml of THF was vacuum transferred from calcium hydride onto the frozen solution of lithium triphenylmethide. The mixture was allowed to come to room temperature and let stir for 15 min. The deep red solution was decanted into the nmr tube, frozen and the tube sealed. Nmr analysis showed only absorptions due to triphenylmethide and triphenylmethane. After addition of D_2O to the contents of the tube, nmr analysis showed the dimers to be absent. On standing the mixture in the tube deposited a dark polymeric substance.

Gas Phase Acidity Studies

Methyl nitrite (135) was prepared in the following manner. A 3-necked 25 ml flask equipped with a magnetic spinbar, dropping funnel, and a gas outlet tube which was connected to a dry ice trap through a gas washing tower filled with 30% aqueous potassium hydroxide and through a calcium chloride drying tube was charged

with 2.38 g of sodium nitrite, 1.50 ml of methanol, and 1.50 ml of water. As the mixture was stirred vigorously, 3.60 ml of a 2:1 water-sulfuric acid mixture was added dropwise. After the addition of each drop of acid, gaseous methyl nitrite bubbled out of the mixture, was freed of acid in the basic wash, was dried in the calcium chloride drying tube and was condensed in the dry ice trap. Methyl nitrite was purified by two trap to trap distillations at atmospheric pressure in which only the middle fraction was collected. The distillation and the strong base wash should remove any possible nitromethane impurity.

Cyclopentadiene was prepared by cracking of its dimer at 180°; triene I was prepared as above; arsine was prepared by Mr. R. Wyatt; all other materials were commercial samples and were used as supplied except for degassing with a freeze-thaw cycle. Impurities in all samples were less than 1%.

An icr cell with overall dimensions of $2.54 \times 1.27 \times 12.7$ cm was employed. An MKS Model 90 H 1-E capacitance manometer was used to determine pressures above 10^{-5} torr. Below 10^{-5} torr pressure was determined from the ion pump current which was assumed to be linear with pressure. Electron energies were measured with a Heath EU-805A digital voltmeter.

Spectral intensities reported in figures were converted to approximate ion abundance by dividing the measured single resonance peak heights by ion mass. Binary mixtures were prepared manometrically.

cis- and trans-XVIII Kinetics

Pyrolyses of cis- and trans-XVIII were carried out in a static reactor of 200 ml volume (Figure 25). The flask is constructed of pyrex glass or quartz and is connected to a vacuum manifold through a section of thick walled capillary tubing and a Teflon stopcock. Dead space in this reactor is less than 1% of the total volume. Fused to the capillary tubing and extending into the center of the flask is a thermocouple well. The manifold includes a small coil trap, 14/20 joint A, vacuum stopcock and 14/20 joint B, vacuum stopcock C, vacuum stopcock and 14/20 joint D and large trap E. System pressure was measured by a mercury manometer at F.

The reaction flask was located in the center of a hollow cavity cylindrical brass block which served as carrier for the heating elements and as an air bath. The block itself was located in a wooden box packed with diatomaceous earth as insulator. The brass block was machined so that the annular volume contained holes for eight General Electric 200 watt immersion heaters. Seven of these heaters were connected in parallel to a 20 amp Variac auto transformer. The eighth heater was connected to a power source through a Bayley proportional controller. Covers with an opening for the section of capillary tubing were fitted to the opening of the brass block and the entire assembly covered by diatomaceous earth up to the opening of the thermocouple well. Temperature was measured by an iron-constatan thermocouple; voltage was read on a Leeds and Northrup

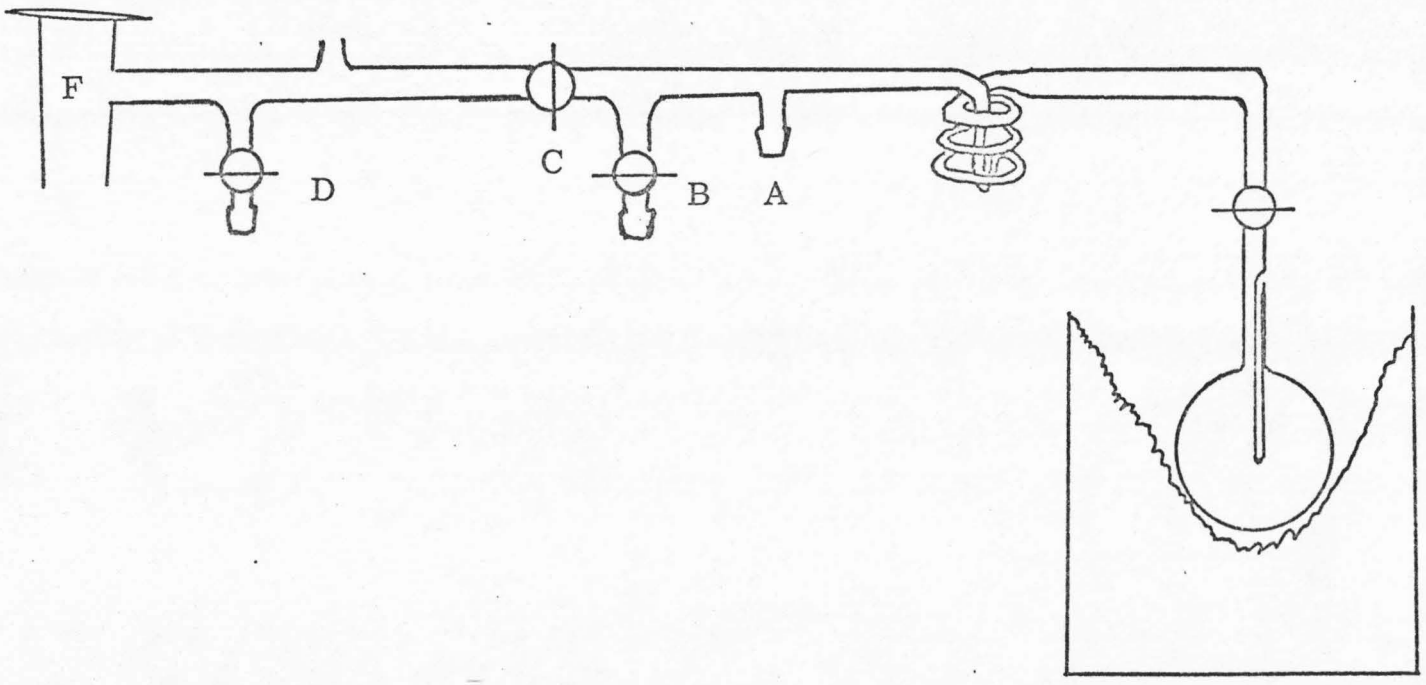


Figure 25. Apparatus for Gas Phase Kinetics

No. 8686 millivolt potentiometer. Temperature could be kept constant during a run to better than ±0.2° and the gradient across the reaction vessel was less than 0.3°.

The reaction vessel was conditioned by heating trans-XVIII for 24 hr at 300°. A typical procedure for obtaining rate constants is the following. The entire system was evacuated to less than 0.05 torr by a Welsh Pump. An appropriate mixture of cis- or trans-XVIII and internal standard (cycloheptane for trans-XVIII and toluene for cis-XVIII) was degassed at joint B (Teflon stopcock closed). The stopcock to the pump was closed and the mixture allowed to vaporize into the manifold. Typically 15-20 torr was obtained. Stopcock B was closed and purified, degassed pentane was vaporized into the manifold from point D to give a total pressure of 110 torr. The Teflon stopcock was opened and the mixture in the manifold allowed to expand into the reaction vessel to give a total pressure of 70 torr. The Teflon stopcock was closed and the remaining vapors in the manifold condensed at A and removed from the line. The system was reevacuated. After the mixture had been in the reaction vessel for 8 to 10 min, stopcock B and C were closed and the Teflon stopcock opened momentarily. The material which expanded into the manifold was condensed with liquid nitrogen at point A. Pentane was distilled into A from D so that the volume of the solution after melting was 50 μl. The aliquot was removed from the line and stored in dry ice until analysis. The system was reevacuated and was ready for the next aliquot at the specified time.

Each aliquot (typically a total of 6 to 8 for each run) was analyzed by injection into glc column H at 40° contained in a Hewlett-Packard Model 5750 gas chromatograph equipped with either a Disc 607 Integrator or a Hewlett-Packard Model 3370A Digital Integrator. The relevant retention times are: trans-XVIII, 7 min; cis-XVIII, 8.8 min; toluene, 10.2 min, cycloheptane 9.1 min, and triene I, 14 min. Each aliquot was analyzed at least three times and the average of the standard/XVIII (A) ratios were recorded for each aliquot. Rate constants were calculated by a least squares program written by Dr. J. Meyer for an Olivetti model programma.

The procedure was exactly the same for a reaction vessel packed with fire polished segments of pyrex tubing in which the surface to volume ratio was increased by a factor of ten.

Low Pressure Pyrolyses

Low pressure pyrolyses in the vacuum flow unit were carried out in the unit given in Figure 23. The procedure was generally the same as that given for the preparation of triene I except that material was passed only once through the hot tube. The product mixtures were analyzed by glc (column H at 45°); the retention times for the relevant species were as follows: trans-XVIII, 6 min; ethynylcyclopentadiene (LVI) 7.8 min; fulvenallene (LV), 9.3 min and triene I, 11.7 min. The Hewlett-Packard model 5750 gas chromatograph and model 3370A Digital Integrator were used to determine product areas. The initial conditions are listed in Tables XV and XVI; the relative

percentages are the averages for three injections for each run. The products of the run listed last in Table XX were analyzed by glc-ms (column H at 40-130°). At least 20 new product peaks were observed in this reaction and their retention times and the mass of the parent peak upon mass spectral analysis are given for the major new components:

Peak (rt)	% mixture	m/e (parent)
B (0.8)	6.2	44
C (1.0)	8.5	56
D (13.5)	2.9	106
F (14.3)	4.1	104
G (16.8)	1.6	120
H (25.0)	0.5	180

Low pressure studies in the static reactor were performed generally in the same manner as the kinetic runs except that pressure was measured by a McLeod gauge attached at joint D, no internal standard was used, and the entire contents of the reaction vessel were withdrawn for analysis at the times specified in Table XVII.

REFERENCES

1. a) D. Ginsburg, ed., "Non-Benzenoid Aromatic Compounds," Interscience, New York, 1959.
   b) D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier, London, 1966.
   c) "Aromaticity," Special Publication No. 21, the Chemical Society, 1967.

2. G. L. Closs, Adv. Alicyclic Chem., 1, 53-127 (1967).

3. A. Streitwieser, Jr. and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, 1965.

4. Reference 1b, p. 55ff.

5. R. Breslow, "Organic Reaction Mechanisms," Second edition, W. A. Benjamin, New York, 1969, p. 14ff.

6. B. A. Hess, L. J. Schaad, J. Amer. Chem. Soc., 93, 301 (1971).

7. O. L. Chapman, C. L. McIntosh, J. Chem. Soc. D, 1971, 770.

8. a) H. Fischer and D. Rewicki, "Progress in Organic Chemistry," 7, 116 (1968).
   b) A. Streitwieser, Jr. and J. H. Hammons, Prog. Phys. Org. Chem., 3, 41 (1965).

9. R. Breslow and W. Washburn, J. Amer. Chem. Soc., 92, 427 (1970).

10. J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, 1962, p. 60.

11. G. V. Boyd, Tetrahedron, 22, 3409 (1966).

12. T. J. Katz, M. Rosenberger, and R. K. O'Hara, J. Amer. Chem. Soc., 86, 249 (1964).

13. R. Bloch, R. A. Marty, and P. deMayo, J. Amer. Chem. Soc., 93, 3072 (1971).

14. H. E. Simmons, "Progress in Physical Organic Chemistry," 7, 1 (1970).

15. A. J. Jones, Rev. Pure Appl. Chem., 18, 253 (1968).

16. D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, 1965, p. 204ff.

17. R. Breslow, W. Washburn, and R. G. Bergman, J. Amer. Chem. Soc., 91, 196 (1969).

18. M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, J. Amer. Chem. Soc., 91, 2378 (1969).

19. a) P. J. Garrat and K. P. C. Vollhardt, J. Chem. Soc. D, 1970, 109.
    b) P. J. Garrat, private communication.

20. W. D. Hunstman and H. J. Wristers, J. Amer. Chem. Soc., 89, 342 (1967). For a complementary study, see B. A. W. Coller, M. L. Hefferman, and A. J. Jones, Aust. J. Chem., 21, 1807 (1968).

21. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Academic Press, 1970.

22. a) L. Skattebøl and S. Solomon, J. Amer. Chem. Soc., 87, 4506 (1965).
    b) H. Hopf, Chem. Ber., 104, 95 (1971).

23. G. H. Mitchell, F. Sondheimer, J. Amer. Chem. Soc., 91, 7520 (1969).

24. N. L. Bauld, C. E. Dahl, and Y. S. Rim, J. Amer. Chem. Soc., 91, 2787 (1969).

25. W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964.

26. a) T. F. Rutledge, "Acetylenic Compounds," Reinhold, New York, 1968, p. 22.
    b) G. Köbrich and P. Buch in "Chemistry of Acetylenes," ed. H. G. Viehe, Dekker, 1969, p. 99.

27. R. J. Crawford, A. Mishra, and R. J. Dummel, J. Amer. Chem. Soc., 88, 3959 (1966).

28. H. D. Hartzler, J. Amer. Chem. Soc., 83, 4990 (1961).

29. a) P. S. Skell, and J. Klebe, J. Amer. Chem. Soc., 82, 247 (1960).
b) R. A. Bernheim, R. J. Kenpf, J. V. Gramas, and P. S. Skell, J. Chem. Phys., 43, 196 (1965).

30. J. V. Gramas, Ph. D. Dissertation, "Triplet States of Bivalent Carbon," Pennsylvania State University, 1965.

31. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, Oxford, 1969.

32. J. Cymerman-Craig and M. Moyle, Proc. Chem. Soc., 1962, 149.

33. H. I. Jacobson, M. J. Griffen, S. Preis, and E. V. Jensen, J. Amer. Chem. Soc., 79, 2608 (1957).

34. I. J. Borowitz, M. Anschel, and S. Firstenberg, J. Org. Chem., 32, 1723 (1967).

35. M. Hanack and H. Eggensherger, Chem. Ber., 96, 1341 (1963).

36. D. R. Kelsey, private communication.

37. a) P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, J. Res. Natl. Bur. Stad., 52, 5 (1954).
b) T. L. Jacobs, Org. Reactions, 5, 1 (1949).

38. L. L. McCoy, J. Amer. Chem. Soc., 80, 6568 (1958).

39. R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, New York, 1967, p. 106.

40. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen, New York, 1964, p. 138.

41. M. S. Newman and G. Kaugars, J. Org. Chem., 31, 1378 (1966).

42. L. Hormer, H. Oediger, and H. Hoffmann, Ann., 626, 26 (1959).

43. R. M. Dodson, and A. Klose, Chem. Ind., 1963, 450.

44. R. W. Murray and A. M. Trozzalo, J. Org. Chem., 27, 3341 (1962).

45. J. Hine, E. L. Pollitzer, and H. Wagner, J. Amer. Chem. Soc., 75, 5607 (1953).

46. P. Yates, Adv. Alicyclic Chem., 2, 60 (1968).

47. K. Hafner, G. Schultz, and K. Wagner, Ann., 678, 39 (1964).

48. A. P. terBorg and A. F. Bickel, Rec. Trav. Chim., 80, 1217 (1961).

49. M. Neuenschwander, R. Kyburz, and R. Iseli, Chimia, 24, 342 (1970).

50. a) W. Parham, H. E. Reiff, and P. Swartzentruber, J. Amer. Chem. Soc., 78, 1437 (1956).
b) W. Parham, and H. E. Reiff, ibid., 77, 1177 (1955).
c) W. Parham and R. R. Twelves, J. Org. Chem., 22, 730 (1957).

51. J. W. Engelsma, Rec. Trav. Chim., 84, 187 (1965).

52. H. L. Rice and T. E. Londergon, J. Amer. Chem. Soc., 77, 4678 (1955).

53. E. R. Alexander, A. B. Herrith, and T. M. Rodes, J. Amer. Chem. Soc., 72, 2760 (1950).

54. A. Streitwieser, Jr., W. B. Hollyhead, G. Sonnicksen, A. H. Pudjaatmaka, C. J. Chang, and T. L. Kruger, J. Amer. Chem. Soc., 93, 5096 (1971) and preceding papers.

55. Reference 16, p. 19.

56. H. Dauben, and M. Rifi, J. Amer. Chem. Soc., 85, 3041 (1963).

57. However, see discussion of Chapter IV for discussion of the relation of anion stability to acidity.

58. J. B. Brutzner and S. Winstein, J. Amer. Chem. Soc., 90, 6562 (1968).

59. a) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, Tetrahedron Lett., 199, 204 (1967).
b) R. B. Bates, S. Brenner, W. H. Deiner, D. A. McCombs, and D. E. Potter, J. Amer. Chem. Soc., 92, 6345 (1970).
c) R. B. Bates, and D. A. McCombs, Tetrahedron Lett. 1969, 977.

60. R. B. Bates, W. H. Deiner, D. A. McCombs, and D. E. Potter, J. Amer. Chem. Soc., 91, 4608 (1969).

61. Chemical and Engineering News, 45, May 22, 1967, p. 54.

62. G. Wilkinson, Organic Syntheses, Coll. Vol. IV, 473 (1963).

63. J. J. Eisch and W. C. Kaska, J. Org. Chem., 27, 3745 (1962).

64. S. Bank and B. Bockrath, J. Amer. Chem. Soc., 93, 430 (1971).

65. a) H. Kloosterziel, Rec. Trav. Chim., 86, 807 (1967).
b) H. Kloosterziel, and J. A. A. VanDrunen, Rec. Trav. Chim., 89, 368 (1970).

66. E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, J. Chem. Soc., 1965, 2997.

67. Reference 16.

68. Reference 16, p. 91.

69. M. Szwarc, Nature, 178, 1168 (1956).

70. R. Waack and M. A. Doran, J. Organometal. Chem., 3, 92 1965.

71. Reference 16, p. 32.

72. J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 92, 5986 (1970).

73. J. D. Baldeschwieler, Science, 159, 263 (1968).

74. D. K. Bohme and L. B. Young, J. Amer. Chem. Soc., 92, 3301 (1970).

75. L. Friedman, Adv. Chem. Ser., No. 58, 199 (1966).

76. J. D. Baldeschwieler and S. S. Woodgate, Acct. Chem., Res., 4, 3301 (1970).

77. M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., J. Amer. Chem. Soc., 93, 4314 (1971).

78. J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 93, 3911 (1971).

79. a) J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 90, 5636 (1968).
b) J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 93, 4316 (1971).

80. D. K. Bohme, 19th Annual Conference on Mass Spectrometry and Allied Topics, Atlanta, Georgia, May 2-7, 1971.

81. D. Holtz, J. L. Beauchamp and J. R. Eyler, J. Amer. Chem. Soc., 92, 7045 (1970) and references cited therein.

82. J. L. Beauchamp and S. E. Buttrill, Jr., J. Chem. Phys., 48, 1787 (1968).

83. K. Jaeger and A. Henglein, Z. Naturforsch. A, 22, 700 (1967).

84. R. N. Compton and L. G. Christopharou, Phys. Rev., 154, 110 (1967).

85. M. Halmann and I. Platzner, J. Phys. Chem., 73, 4376 (1969).

86. R. H. Wyatt, Masters Thesis, California Institute of Technology, 1971.

87. P. Potzinger and F. W. Lampe, J. Phys. Chem., 73, 3912 (1969) report 6.7 ev.

88. C. D. Ritchie and R. Uschold, J. Amer. Chem. Soc., 90, 2821 (1968).

89. a) R. G. Bergman and W. L. Carter, private communication reporting 17 kcal/mole stabilization energy for the cycloheptadienyl radical.
b) S. Furuyama, D. M. Golden, and S. W. Benson, Intl. J. Chem. Kinetics, 3, 237 (1971).

90. C. D. Ritchie, J. Amer. Chem. Soc., 91, 6749 (1969).

91. a) J. Hine, J. Org. Chem., 31, 1236 (1966).
b) J. Hine, J. Amer. Chem. Soc., 88, 5525 (1966).

92. J. L. Beauchamp and J. Cooke, private communication.

93. K. C. Smythe, R. T. McIver, Jr., J. I. Brauman, and R. W. Wallace, J. Chem. Phys., 54, 2758 (1971).

94. S. W. Benson, J. Chem. Ed., 42, 503 (1965).

95. Table X, reference d.

96. a) E. Vogel, Angew. Chem., 74, 829 (1962).
b) As reported in reference 102, p. 163.

97. G. S. Hammond and C. D. DeBoer, J. Amer. Chem. Soc., 86, 899 (1964).

98. C. S. Elliot and H. M. Frey, J. Chem. Soc., 1964, 900.

99. K. W. Egger, S. A. Golden, and S. W. Benson, J. Amer. Chem. Soc., 86, 5421 (1964).

100. M. M. Martin and E. B. Sanders, J. Amer. Chem. Soc., 89, 3777 (1967).

101. G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, New York, 1955.

102. H. M. Frey, Adv. Phys. Org. Chem., 4, 147 (1966).

103. The situation is qualitatively similar to bimolecular reactions where A factors are typically low; see reference 112, p. 96ff.

104. W. F. Anderson, J. A. Bell, J. M. Diamond, and K. R. Wilson, J. Amer. Chem. Soc., 80, 2384 (1958).

105. B. J. Rabinovitch and K. W. Michel, J. Amer. Chem. Soc., 81, 5065 (1959).

106. G. B. Kistiakowsky and W. R. Smith, J. Amer. Chem. Soc., 58, 766 (1936).

107. B. Tamamushi, H. Akiyama and K. Ishii, Zert. Electrochem., 47, 340 (1941).

108. L. D. Hawton and G. P. Semeluk, Can. J. Chem., 44, 2143 (1966).

109. T. H. Morton, personal communication.

110. D. W. Setser, and B. S. Rabinovitch, Can. J. Chem., 40, 1425 (1962).

111. a) P. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, J. Amer. Chem. Soc., 92, 2147 (1970).
b) E. Hedaya and M. E. Kent, ibid., 2149.

112. S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, New York, 1968.

113. S. W. Benson, personal communication.

114. T. J. Henry, personal communication.

115. R. G. Bergman, personal communication.

116. H. M. Frey, Trans. Faraday Soc., 58, 516 (1962).

117. Saul Dushman, J. M. Lafferty, eds., "Scientific Foundations of Vacuum Technique," John Wiley & Sons, New York, 1962, p. 30.

118. S. C. Chan, B. S. Rabinovitch, J. J. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lin, and S. P. Pavlou, J. Phys. Chem., 74, 3160 (1970) and references cited therein.

119. R. C. Joines, A. B. Turner, and W. M. Jones, J. Amer. Chem. Soc., 91, 7754 (1969).

120. A. P. ter Borg and H. Kloosterziel, Rec. Trav. Chim., 88, 266 (1969) and preceding papers.

121. A. deRay, H. Monti, M. Bertrand, and H. Bodot, Bull. Soc. Chim. France, 1968, 1450.

122. L. Vo-Quang and P. Cadiot, Bull. Soc. Chim. France, 1965, 1518.

123. L. Vo-Quang and M. Simonin, Bull. Soc. Chim. France, 1965, 1929.

124. a) L. F. Fieser and D. H. Sachs, J. Org. Chem., 29, 1113, (1964).
b) M. C. Flowers and H. M. Frey, J. Chem. Soc., 1962, 1689.

125. a) J. Van der Keck, J. Appl. Chem., 7, 367 (1957).
b) W. R. Cullen and G. E. Styan, J. Organometal. Chem., 6, 117 (1966).
c) R. M. Fantazier and M. L. Poutsma, J. Amer. Chem. Soc., 90, 5490 (1968).
d) D. Seyferth, H. Yamazaki, and D. L. Alleston, J. Org. Chem., 28, 703 (1963).

126. L. Vo-Quang, Compt. Rend. (C), 266, 642 (1968).

127. W. H. Okamura and F. Sondheimer, J. Amer. Chem. Soc., 89, 5991 (1967).

128. F. Schulte, Arch. Pharm., 299, 107 (1966).

129. J. Werner, J. Chem. Soc., 115(2), 1096 (1919).

130. E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 87, 1345 (1965).

131. Personal observation of R. G. Bergman.

132. F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, 1969.

133. Reference 31, p. 283.

134. W. G. Dauben and R. L. Cargill, Tetrahedron, 12, 186 (1961).

135. P. Gray, Proc. Roy. Soc. (A), 232, 389 (1955).